QD
133
U7

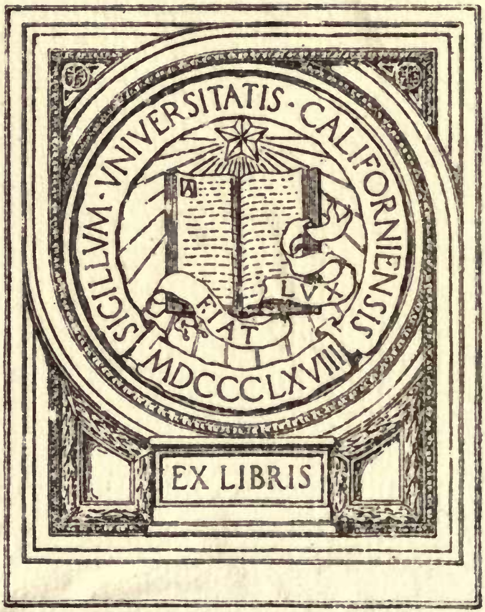
UC-NRLF

$B 622 373

United States Steel Corporation

METHODS FOR THE COMMERCIAL SAMPLING AND ANALYSIS OF ALLOY STEELS

GIFT OF



SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
FIAT LVX
MDCCCLXVIII
EX LIBRIS

METHODS

OF THE

CHEMISTS' COMMITTEE

OF THE

UNITED STATES STEEL CORPORATION

FOR THE

ANALYSIS OF ALLOY STEELS

UNIV. OF
CALIFORNIA

G388MCC115

QD133
U7

Gift of
Carnegie Steel Co

COPYRIGHT, 1915,
BY
J. M. CAMP,
CHAIRMAN CHEMISTS' COMMITTEE

UNIV. OF CALIFORNIA

CONTENTS.

	Page.
PREFACE	7
SAMPLING	8
Preparation of Samples as Plain Steels	8
Number of Tests to be taken	8
Securing the Test	8
Cooling the Test	8
Preparation of the Sample	8
Preparation of Samples—Special Steels	9
Annealing the Test and Preparing the Sample	9
LADLE TEST MOULD No. 1	10
LADLE TEST MOULD No. 2	11
QUALITATIVE TESTS	12
METHODS OF ANALYSIS	15
General Remarks	15
DETERMINATION OF CARBON	16
Direct Combustion	16
Rapid Oxidation Method	17
Slow Oxidation Method	18
Increase in Weight of Potash Bulb and Dehydrating Tubes	18
Solutions Required	18
Filtration and Ignition of the Barium Carbonate	19
Titration of the Excess Barium Hydroxide	19
Solutions Required	21

320978

PAGE.

DETERMINATION OF MANGANESE........................ 22
  Ford's Method........................ 22
  Sodium Bismuthate Method. Absence of Chromium........ 24
    Solutions Required........................ 25
  Modified Bismuthate Method........................ 25
    Solution Required........................ 26
  Zinc Oxide Separation. Presence of Tungsten........... 26
    Color Method........................ 26
    Sodium Arsenite Titration........................ 26
    Solutions Required........................ 27

DETERMINATION OF PHOSPHORUS........................ 28
  Volumetric Methods. Absence of Tungsten, Vanadium and Titanium........................ 28
    Acid-Alkali Titration........................ 28
    Solutions Required 29
  Potassium Permanganate Titration........................ 30
    Solutions Required........................ 31
  Gravimetric Method. Absence of Tungsten, Vanadium and Titanium........................ 31
    Weighing as Ammonium Phosomolybdate........................ 31
    Weighing as Magnesium Pyrophosphate........................ 32
    Solutions Required........................ 33
  Presence of Vanadium. Absence of Tungsten and Titanium 33
  Presence of Tungsten. Absence of Titanium.............. 34
  Presence of Titanium. Absence of Tungsten and Vanadium 35
    Fusion Method........................ 35
  Presence of Titanium, Tungsten and Vanadium.............. 36

DETERMINATION OF SULPHUR........................ 37
  Volumetric Method........................ 37
    Solutions Required........................ 38
    Absorbents Required........................ 39
  Gravimetric Method. Presence of Tungsten and Molybdenum........................ 39

DETERMINATION OF SILICON........................ 42
  Sulphuric Acid Method. Absence of Tungsten........... 42

DETERMINATION OF SILICON AND TUNGSTEN........... 43

PAGE.

DETERMINATION OF TUNGSTEN 44
Rapid Method 44

DETERMINATION OF CHROMIUM 45
Chlorate Method 45
Solutions Required 46
Permanganate Oxidation Method. Presence of Tungsten 46
Permanganate Oxidation Method. Absence of Tungsten 47

DETERMINATION OF CHROMIUM AND VANADIUM 48
Persulphate Method 48
Solutions Required 49

DETERMINATION OF VANADIUM 51
Volumetric Method. Absence of Tungsten 51
Ether Separation 51
Solutions Required 52
Phosphomolybdate Precipitation 52
Solutions Required 53
Color Method. Absence of Titanium 53
Solutions Required 54

DETERMINATION OF NICKEL 55
Volumetric Method. Absence of Copper and Cobalt 55
Solutions Required 56
Glyoxime Method 56
Weighing the Precipitate 57
Weighing as Nickel Oxide 58
By Titration 58
Solutions Required 58

DETERMINATION OF COBALT (Ni.) 59
Sulphide Precipitation 59
Nitroso-β-Naphthol Method 60

DETERMINATION OF COPPER. Absence of Molybdenum 62
Gravimetric Method 63
Volumetric Method 63
Solutions Required 64
Presence of Molybdenum 64

PAGE.
DETERMINATION OF MOLYBDENUM 65
Gravimetric Methods 65
Weighing the Molybdenum Trioxide 65
Weighing as Lead Molybdate 65
Volumetric Method 66
Solutions Required 66

DETERMINATION OF ALUMINUM 67

DETERMINATION OF TITANIUM 69
Color Method. Absence of Vanadium, Chromium, Tungsten, Molybdenum and Nickel 69
Solutions Required 69
Gravimetric Method 70

PREFACE.

The demand for special or alloy steels has, during the last few years, increased to such a degree that, in place of being made by a few manufacturers in a very limited quantity and for very limited purposes, practically every steel works has been called upon to furnish this material in large quantities and in an ever increasing number of varieties.

The methods used for the determination of the ordinary elements in plain steels cannot, in many instances, be applied to alloy steels because of the interference of the alloying elements. The metals which are generally present in these steels are chromium, tungsten, vanadium, cobalt, nickel, molybdenum and copper.

The Chemists' Committee of the United States Steel Corporation present for their chemists' guidance, this compilation of what it believes to be the most satisfactory methods of analyses for alloy steels to be found at the present time. The compilers make no claims for originality regarding both the methods and the apparatus described, although, in a number of instances, it is believed that new points have been brought out, which should be of interest and value. Since this pamphlet is intended as a guide to the novice, as well as an aid to the more experienced chemist, all methods have been described in detail.

To facilitate the examination of steels of unknown composition, a scheme for making complete qualitative tests has been included.

The Committee of Chemists responsible for this compilation, in addition to the Chairman, consisted of Mr. A. B. Clemence, Chief Chemist of the Worcester, Mass., plant of the American Steel and Wire Company, Mr. John L. Harvey, Chief Chemist of the Homestead Works of the Carnegie Steel Company, and Mr. I. A. Nicholas, Chief Chemist of the Clairton Works of the Carnegie Steel Company, for which service the Chairman of the Committee is pleased to express his thanks.

SAMPLING.

The method of sampling alloy steels is similar to that for plain steels with the exception of high nickel, high manganese, and tungsten or high speed steels, which require special heat treatment before they can be drilled. For all other steels the sampling is conducted as described in the plain steel pamphlet, which method is as follows:

PREPARATION OF SAMPLES AS PLAIN STEELS.

NUMBER OF TESTS TO BE TAKEN:

One test for analysis should be taken from each heat, and that at the time, as near as is practicable, when one-half of it has been poured.

SECURING THE TEST:

A spoon is held under the stopper hole of the ladle, while the stream of molten metal is momentarily slackened, until a sufficient amount of the metal is caught therein. The metal is then poured from the spoon into the test mould.

DESCRIPTION OF THE TEST MOULDS:

Either one of two types of moulds may be used. Mould No. 1 (see print), usually designated as the split mould, consists of two similar parts made of cast iron or steel. The upper part is flared, which acts as a sink head for the molten metal. Two forms of support are shown. The one, a steel plate in which a suitable hole for containing the mould pieces is cut, is supported by two channels riveted to the plate; the other is a form which fits the mould pieces and holds them together. After the test is taken it is allowed to solidify, when the mould and contents are withdrawn from the support. The mould pieces then fall apart and expose the test.

Mould No. 2 (see print) is a one piece casting of iron or steel. It is provided with a threaded hole into which a steel handle is screwed. The test piece is removed by inverting the mould.

COOLING THE TEST:

After the test has been removed from the mould, it is stamped with the furnace and heat number and then delivered to the laboratory, where it is cooled by means of an air blast until it can be readily handled.

PREPARATION OF THE SAMPLE:

The sample is prepared by drilling the test with a ¾″ drill. Test No. 1 is drilled to a point between 1″ and 2½″ from the bottom end of the test and to such a depth as will give a sufficient amount of drillings. The test piece may be drilled through, if necessary. Test No. 2 is drilled on the bottom and to a depth not greater than one inch from the bottom surface of the test. In either case, to prevent contamination from scale, the drillings are discarded, until the outer edge of the drill is buried.

PREPARATION OF SAMPLES—SPECIAL STEELS.

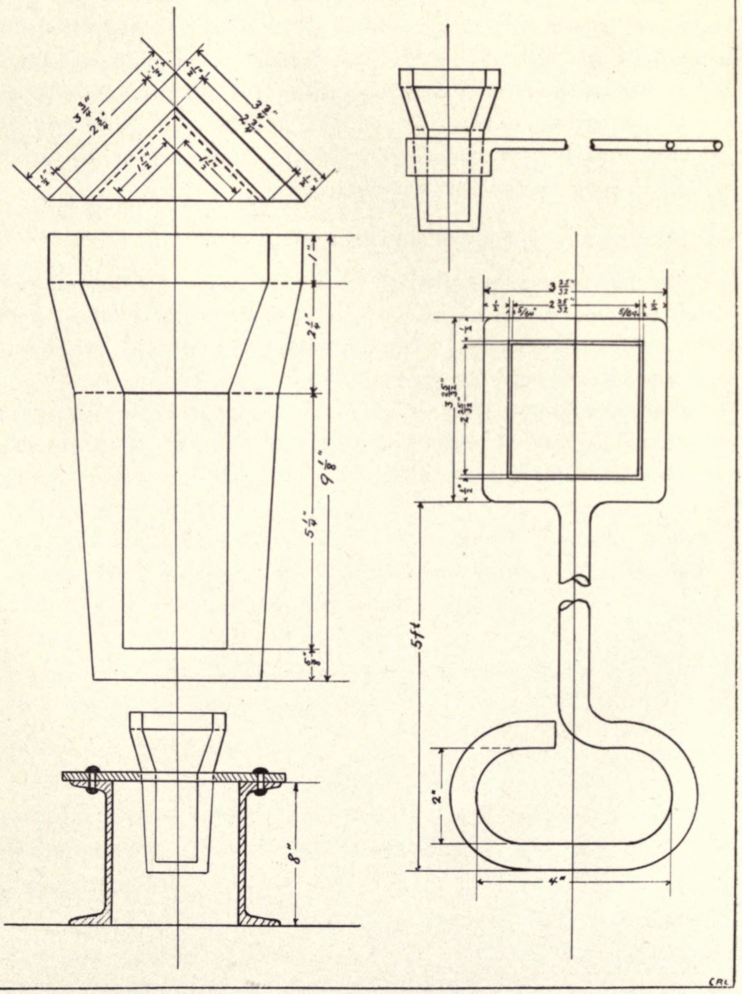
Steel samples containing tungsten must first be annealed before they can be drilled. A sample of steel containing high nickel (5 to 7%) and manganese (approx. 13%) may be obtained by drilling the test—heated to a dull red—with a high speed drill. The drillings are slightly oxidized, but not to such an extent as to materially affect the analysis. A sample can also be obtained by drilling the cold test with a cobalt steel drill which has been properly heat treated. The drillings in this case are not oxidized, and are in good condition for analysis.

ANNEALING THE TEST AND PREPARING THE SAMPLE:

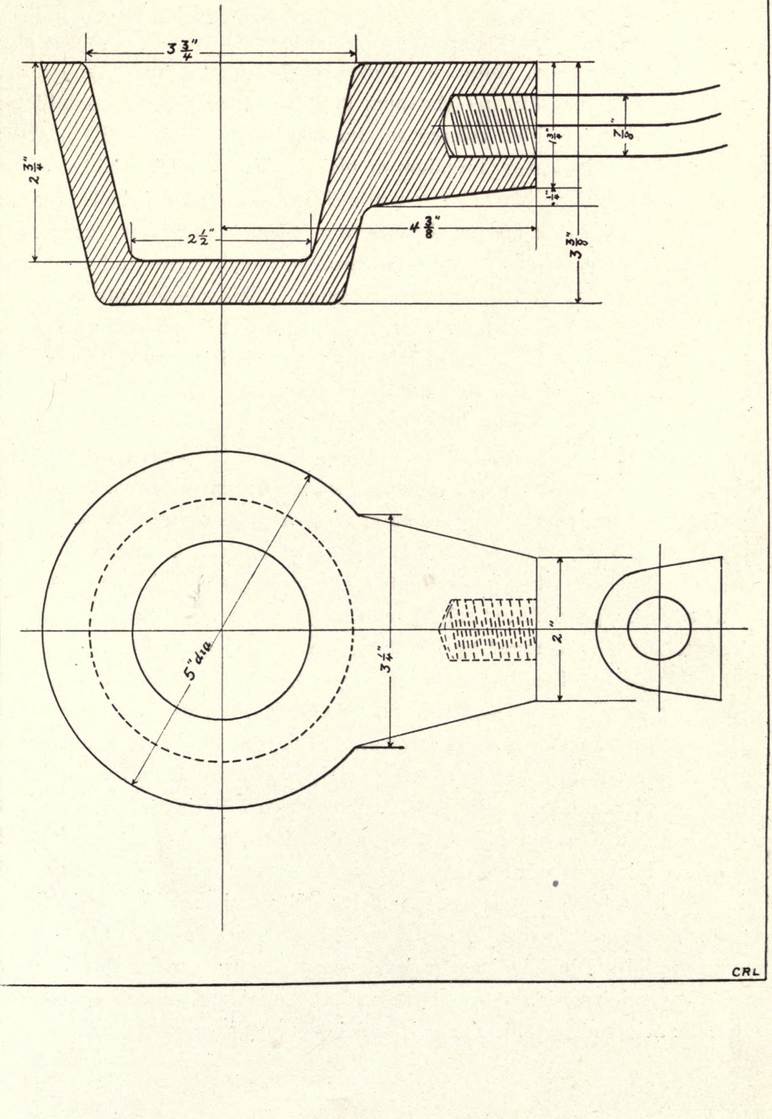
The test piece is transferred to a furnace whose temperature can be closely controlled and is heated for ½ to ¾ of an hour at a temperature of 720°C. After the test is annealed, it is cooled in the air and the sample is obtained in the usual manner by drilling.

It may be advantageous to anneal only a portion of the test piece; in this case it is sheared, while hot, to the desired size, when the smaller piece is annealed as just described.

LADLE TEST MOULD No. 1
(with 2 forms of support)


3 3/4"
2 3/4"
1/2"
1/2"
1 1/2"
1 1/2"
3 3/4"
2 3/4"
1/2"
1/2"
1"
2 1/4"
5 1/4"
9 1/8"
5/8"
8"
3 25/32"
2 25/32"
1/2
5/64"
5/64"
1/2
3 25/32"
2 25/32"
1/2
1/2"
5 ft
2"
4"
CRL

LADLE TEST MOULD No. 2


3 3/4"
2 3/4"
2 1/2"
4 3/8"
1 3/4"
7/8"
1/4"
3 3/8"
5" dia
3 1/4"
2"
CRL

QUALITATIVE TESTS.

A number of the elements encountered in alloy steels may be detected by making a direct test upon the solution of the sample. The presence of tungsten and various other combinations of elements, however, interferes with many of the tests, and in order to provide for the detection of any or all of the elements that may be present in an alloy steel, the following scheme is herewith presented:

One gram of steel is treated with 50 cc. of hydrochloric acid (1.13 sp. gr.). After all action ceases, chromium, nickel, copper, cobalt and titanium are dissolved; while tungsten, molybdenum and vanadium remain insoluble as a black residue. A blue colored solution indicates cobalt, while a green colored solution indicates chromium or nickel. If a black insoluble residue remains, .5 gram of sodium chlorate is added, and the solution is boiled for five minutes. If the black residue changes to a lemon yellow color, tungsten is indicated. If the residue completely dissolves, molybdenum and vanadium are indicated as well as the absence of tungsten. This solution, after dilution with water, may be tested for copper, titanium, molybdenum and vanadium. The insoluble residue suspected of being tungstic acid is removed by filtration and is treated with metallic zinc and hydrochloric acid, whereby tungstic acid is reduced and the solution first becomes blue and then brown. To the filtrate from the tungstic acid, 20 cc. of sulphuric acid (1–1) are added, and the solution is evaporated until fumes of sulphuric anhydride are evolved. The residue is treated with 50 cc. of water and heated gently until the separated salts are dissolved. The solution is diluted to 200 cc., ammonia is added until almost neutral when it is saturated with hydrogen sulphide gas and then boiled until the precipitated sulphides of molybdenum and copper coagulate. The precipitate is removed by filtration, washed and ignited at a very low heat. The oxides of molybdenum and copper are treated while in the crucible with dilute caustic potash solution. The molybdenum oxide is thus dissolved while the copper oxide remains insoluble. The contents of the crucible are filtered and the filtrate may be tested for molybdenum by one of two methods. Either the filtrate is just acidified with dilute hydrochloric acid, and 1 cc. of a 5% solution of mercurous nitrate is added, followed by a few crystals of potassium thiocyanate, when the solution will assume a red color, which will not fade if molybdenum is present; or the filtrate is acidified with dilute sulphuric acid and is then saturated with hydrogen sulphide, when a dark brown precipitate will indicate molybdenum. To test further in the latter case, the precipitate is removed by filtration, ignited and treated with dilute sulphuric acid and metallic zinc. If molybdenum is present, the solution will be colored first blue, then green, and finally brown. The insoluble black residue of copper oxide is dissolved in strong nitric acid, the solution is diluted with water, and ammonia is added in excess. A blue color indicates copper.

To detect vanadium and titanium, the filtrate from the sulphides of molybdenum and copper is concentrated to a volume slightly less than 100 cc., when a solution of potassium permanganate is added in slight excess. The solution is boiled for a few minutes and cooled to room temperature. Ten cc. of hydrogen peroxide are then added, the solution is diluted to 100 cc. and is then divided into two equal portions which are transferred to No. 2 beakers. If titanium alone is present the solutions are colored yellow, if vanadium alone is present the solutions are colored a deep brown, if both elements are present the brown color due to the presence of vanadium is readily distinguished, while to detect titanium, one drop of hydrofluoric acid is added to one solution, whereby the yellow color due to titanium will be destroyed. This solution is then compared with the solution to which no hydrofluoric acid has been added and if a change of color is observed titanium is indicated.

For the detection of chromium, nickel and cobalt in the presence of tungsten, another solution of the sample is prepared as follows: One gram of steel is transferred to a No. 2 beaker, 100 cc. of hydrochloric acid (1-1) are added and the contents of the beaker are boiled until all action ceases. The volume of the solution should now be about 50 cc. An equal volume of water containing .5 gram of sodium chlorate is then added and the solution is boiled for five minutes. The tungsten is thus converted to tungstic acid, is separated by filtration and then discarded. In order to remove the excess of iron from the filtrate, an ether separation is made as follows: 3 cc. of nitric acid (1.20 sp. gr.) are added and the solution is rapidly evaporated to about 40 cc., cooled to room temperature and transferred with hydrochloric acid (1.11 sp. gr.) to a separatory funnel. The volume should not exceed 50 cc. Thirty cc. of ether are added, the funnel is well shaken, and the lower liquid containing but a trace of iron and molybdenum and all the other elements is run into a beaker. The solution is gently heated to expel traces of ether, 20 cc. of sulphuric acid (1–1) are added and the contents of the beaker are evaported until fumes of sulphuric anhydride are evolved. After cooling, 50 cc. of water are added to the beaker and, when the separated salts have dissolved, any copper or molybdenum which may be present are precipitated by hydrogen sulphide gas as previously described. The precipitated sulphides are removed by filtration, and the filtrate is boiled to expel the excess of hydrogen sulphide. To one-half the solution is then added one-fourth its volume of strong nitric acid followed by an excess of a concentrated solution of potassium permanganate. The solution is boiled for ten minutes, and if it is colored yellow, chromium is indicated. This solution may be tested further for chromium by transferring 20 cc. to a test tube containing 5 cc. of hydrogen peroxide. The yellow chromate solution will change to blue and upon shaking the solution with ether, the latter will withdraw the chromium compound and will be colored blue. The remaining half portion of the solution is treated with 5 grams of citric acid, and, after making strongly alkaline with ammonia, the solution is saturated with hydrogen sulphide, whereby the cobalt and nickel together with iron and manganese will be precipitated as sulphides. The precipitate is removed by filtration, carefully ignited in a platinum crucible, transferred to a beaker and dissolved in strong hydrochloric acid. The solution is then made slightly ammoniacal, about one-half gram of ammonium persulphate is added and the solution is boiled and filtered to remove oxides of iron and manganese. The filtrate containing the nickel and cobalt is divided into two portions; to one portion 5 cc. of a one per cent alcoholic solution of dimethylglyoxime are added and if a bright red precipitate is formed, nickel is indicated. The remaining portion of the filtrate is slightly acidified with dilute hydrochloric acid, heated to boiling, and a freshly prepared solution of nitroso β naphthol is added. The nitroso β naphthol is made by dissolving about ½ gram of the reagent in 10 cc. of hot acetic acid (75%). After the addition of this solution, the contents of the beaker are boiled for a few minutes, when cobalt, if present, is precipitated as a red colored compound, together with some excess of the reagent. The solution is filtered, while hot, and the paper ignited in a porcelain crucible, whereby cobalt will be converted to the oxide. The residue in the crucible is treated with hydrochloric acid whereby the cobalt will be dissolved, coloring the solution blue. This solution may be tested further by adding ammonia, when the solution will be colored pink if cobalt is present.

METHODS OF ANALYSIS.

GENERAL REMARKS.

In the following directions for the analysis of alloy steels, it has been the desire to give the methods in considerable detail. In order to avoid constant repetition, however, the following statements are made herewith:

Whenever water is mentioned as a reagent, it is understood to mean distilled water. The strength of acids is indicated by the word "strong" or by the proportion, by volume, of strong acid to water in parenthesis. The word "strong" signifies that the ordinary concentrated acid and ammonia as received from the manufacturer is used. The specific gravities of sulphuric, nitric, hydrochloric acids and ammonia water would thus be 1.84, 1.42, 1.19 and .90, respectively. In giving the proportions in parenthesis the proportion of water is always given last. It is understood that not only the acids, but all the chemicals mentioned must be of C. P. grade.

A number of the methods cannot be used for the analysis of every combination of an alloy steel, as the presence of certain elements may interfere with a method as described. In this case, to the right of the heading for each method will be found a statement showing what elements interfere with the method as described, e. g. "Absence of Tungsten" signifies that the method cannot be used if tungsten is present. Should there be no statement, it may be concluded that none of the alloying elements interfere. As some of the methods are especially applicable when certain elements are present, a statement to this effect will also be made, e. g. "Presence of Tungsten" signifies that the presence of any of the other elements unless specified, does not interfere, and that the method is especially applicable when tungsten is present.

DETERMINATION OF CARBON.

DIRECT COMBUSTION.

Owing to the fact that the colors of the solutions obtained by dissolving alloy steels in nitric acid are such that accurate determinations cannot be made by the color method, as in plain steels, the combustion method must be used. The method to be recommended is the direct combustion, for which purpose the drillings should be as small as possible, that portion passing through a 20 mesh sieve and retained in a 40 mesh sieve should be used A temperature of 1000°C. should be maintained for the combustion of all steel samples, except those containing a high percentage of tungsten, which require a slightly higher temperature.

The combustion is conducted preferably in a fused quartz tube (24″x⅞″) for which heat is furnished by a suitable gas or electric furnace. A platinum tube may also be used, but on account of greater expense and possibility of damage by oxidized iron, the quartz will be found more practical. In either case, however, the insertion of a thin platinum sleeve in the combustion zone will prolong the life of the tube.

For the operation of the electric furnace, equipped with a rheostat, either a direct or alternating current may be used. The alternating current, however, proves more satisfactory in that the high temperature required can be attained more readily, and the high resistance wire does not burn out so quickly, provided the furnace is properly equipped with a transformer. For the exact regulation of the temperature, a pyrometer will be found necessary.

The container for the sample is a boat made of clay, nickel, alundum, porcelain or platinum. The boat, of whatever material, is protected from the sample by means of a layer of emery or alundum, and before using, both must be ignited for a length of time sufficient to free them from carbonaceous matter. The following dimensions for the boat will be found convenient, length 3″ to 3½″, depth ¼″, width at bottom ½″, width at top ⅝″.

The oxygen contained in a high pressure cylinder provided with a reducing valve, is purified by being conducted through a wash bottle containing caustic potash solution (50%). It then enters the combustion tube through a glass tube held in position by a perforated rubber stopper. In order to prevent radiation of heat, a copper disk or a plug of asbestos enclosed in platinum gauze is inserted in the tube; or a small water jacket may be used to keep the end of the tube cool. In the center of the hot zone is the boat containing the sample. Here partially or completely the gas combines with the steel, while the portion escaping, together with the generated carbon dioxide and oxidized sulphur, is forced through loosely packed asbestos extending from the center of the hot zone to the end of the combustion tube. The asbestos serves two purposes; in the hot zone it acts as a catalizer and insures the complete oxidation of carbon monoxide to carbon dioxide, while at the exit end of the tube it prevents radiation of heat. In order to insure the removal of the oxidized sulphur, a small glass tube containing a small quantity of granulated zinc is connected to the combustion tube by means of a perforated rubber stopper. The gases are thereby conducted to the absorption vessel, where the carbon dioxide may be disposed of in several different ways; the operator also has the choice of one of two methods for oxidizing the sample.

RAPID OXIDATION METHOD.

A depression in the shape of a "V" about one inch long is made in the refractory material contained in the combustion boat, and one gram or a convenient weight of the sample, depending upon the manner of absorbing the carbon dioxide, is transferred thereto. The sample is placed as compactly as possible, whereby the heat of oxidation of the steel is so conserved that a complete fusion of the oxidized iron results. The absorption apparatus is attached to the glass tube at the exit end of the combustion tube, the rubber stopper removed at the entrance end, and the boat quickly placed in the center of the combustion zone. The plug and stopper are instantly replaced, and the precaution taken that all connections are tight. The oxygen is then admitted at such a rate that a continuous bubbling is observed in the absorption vessel.

In the course of one minute, the steel will begin to oxidize, and the rate of bubbling in the absorption vessel will decrease. When the steel is completely oxidized, a sudden acceleration of the bubbling in the absorption vessel will occur. At this point, in order to completely expel the carbon dioxide from the combustion tube, the rate of flow of oxygen is regulated depending upon the absorbent solution used. If barium hydrate is used as an absorbent, the flow of oxygen is reduced to a rate of three bubbles per second and so maintained for 10-15 minutes. If caustic potash is used, the flow of oxygen may either be maintained at the original rate or slightly reduced depending upon the type of absorption vessel, and is so maintained for 5-10 minutes. The absorption vessel is then disconnected, the current of oxygen discontinued and the analysis concluded by any of the methods hereinafter described.

Slow Oxidation Method.

This method differs from the preceding one only in the manner in which the sample is contained in the boat, and the rate in which the oxygen is admitted to the combustion tube. In the former method, the sample is fused, while in this method, the steel particles are completely oxidized yet retain their original shape.

The sample is spread out loosely over the surface of the refractory material contained in the boat and the oxygen is admitted to the combustion tube at a rate not exceeding 3 bubbles per second. The flow of oxygen is then continued for 30 minutes, when it is discontinued and the carbon dioxide is disposed of by any one of the following methods:

INCREASE IN WEIGHT OF POTASH BULB AND DEHYDRATING TUBE

Since appreciable amounts of water are vaporized from the potash bulb, it must be followed by and weighed with a calcium chloride or preferably phosphoric anhydride tube. Consequently, in order to remove traces of aqueous vapor from the gases before entering the absorption bulb, it is preceded by a similar dehydrating tube which is not weighed with the absorption apparatus. For the sake of convenience the latter dehydrating tube may contain the small quantity of zinc used for removing the oxidized sulphur and is connected directly with the combustion tube by means of a perforated rubber stopper.

The absorption tube and the accompanying dehydrating tube are connected to the combustion train and a current of oxygen is passed through to the complete expulsion of air, and the combined weight of the absorption bulb and dehydrating tube noted. They are again placed in position, and the combustion carried out as above described. Each one-tenth milligram increase in weight represents .0025 per cent carbon when an initial weight of 1.0909 gram—4 times the factor weight—is used.

Solution Required.

Caustic Potash Solution (50%).

Caustic Potash	500 grams.
Water	1000 cc.

FILTRATION AND IGNITION OF THE BARIUM CARBONATE.

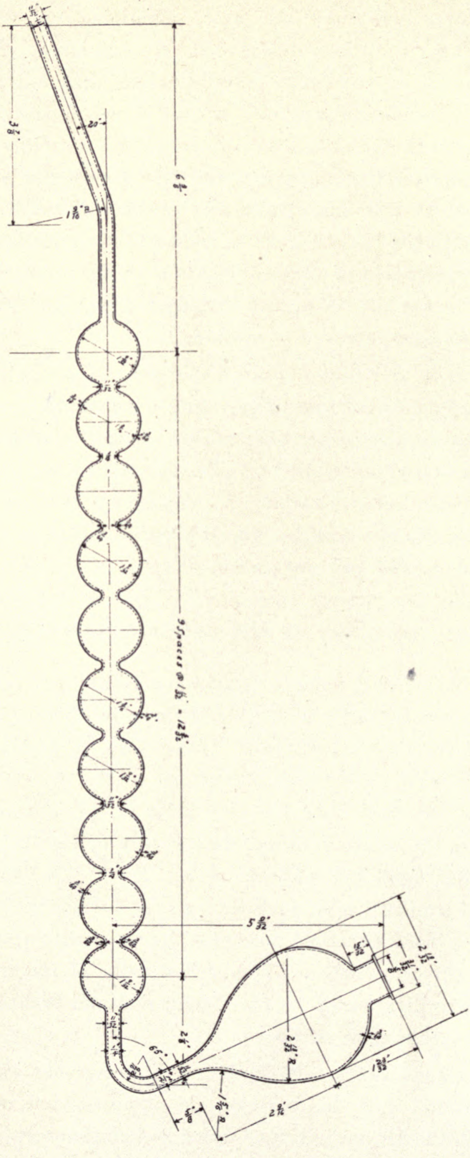
A Meyer bulb tube (see print) containing 100 cc. of barium hydrate solution (2 per cent) is attached to the combustion apparatus. The combustion is conducted as already described, but, since barium hydrate does not absorb carbon dioxide as readily as caustic potash, the gases should therefore be conducted through the absorbent solution less rapidly. After the combustion is completed the contents of the tube are filtered with moderate suction through an 11 cm. filter paper and washed with water, free from carbon dioxide, until the barium hydrate is completely removed. In order to minimize the absorption of carbon dioxide from the air, it is recommended that the filter be not allowed to run dry, until the greater portion of the original solution has been removed by washing.

The filter and contents are transferred to a weighed platinum crucible and ignited at a moderate temperature until the filter paper disappears and finally at a slightly higher temperature for five minutes. The weight of the barium carbonate multiplied by 6.08 and divided by the initial weight used, is equivalent to per cent carbon. A convenient initial weight is 1.216 gram—2 times the factor weight—whereby each milligram of barium carbonate corresponds to .005 per cent carbon.

TITRATION OF THE EXCESS BARIUM HYDROXIDE.

The Meyer bulb tube is detached as before, its contents are transferred to a 12 ounce Erlenmeyer flask, and the tube thoroughly washed with cold water free from carbon dioxide. Three drops of phenolphthalein solution are added, followed by successive portions of the standard acid with violent shaking of the flask until the pink color of the indicator disappears. The agitation of the solution insures the recovery of any carbon dioxide that may be liberated upon the addition of the acid. The difference between the amount of standard acid, equivalent to the barium hydroxide used, as determined by a blank titration, multiplied by the carbon value of the acid corresponds to per cent carbon. The carbon value of the standard acid may be conveniently determined by the combustion and titration of one gram of a standard steel as outlined above.

The blank titration is conducted in a manner identical to an actual determination. For this purpose, the same amount of absorbent solution is placed in the Meyer bulb tube which is then connected with the combustion apparatus. Oxygen is passed through the apparatus for the same length of time as required for an actual determination. The tube is then detached, its


11/32"
3 7/8"
20°
1 9/16" R
6 3/8"
9 Spaces @ 1 11/32" = 12 3/32"
5 9/32"
2 3/8"
65°
2 11/32" R
2 11/32"
1 23/32"
2 9/16"
1 5/16" R
5/8"
15/32"

contents are transferred to a 12 ounce Erlenmeyer flask, and the indicator is added followed by standard acid until the pink color disappears.

Solutions Required.

Standard Hydrochloric Acid.

Hydrochloric Acid (1.19 sp. gr.)	8 cc.
Water	1000 cc.

The water used should be free from carbon dioxide. One cc. of this solution is equivalent to approximately .05 per cent carbon on a basis of an initial weight of one gram of the sample.

Barium Hydroxide Solution.

Barium Hydrate	20 grams.
Water	1000 cc.

The water used should be freshly boiled. When the solution has reached room temperature, it is filtered through a 25 cm. filter paper as rapidly and carefully as possible. The solution, protected by a guard tube filled with soda lime or caustic potash solution, is conveniently withdrawn from the container by means of a suitable syphon.

Phenolphthalein Solution.

Phenolphthalein	1 gram.
Ethyl Alcohol	1000 cc.

DETERMINATION OF MANGANESE

FORD'S METHOD.

For the determination of manganese, Ford's method is credited with being the most accurate of the gravimetric methods. A number of sources of error, tending to make the results of analysis too high, are, nevertheless, involved unless special precautions to prevent them are observed. Among these may be mentioned the danger of contamination from the glass-ware and asbestos used in making a determination, and the fact that, even with unusual care in the final precipitation, the manganese pyrophosphate is sometimes found to vary slightly in composition. However, the method is sufficiently nearly accurate to warrant its use for the determination of manganese in the standards employed in the subsequently described methods.

Three to five grams of the sample are transferred to a No. 4 beaker provided with a cover glass, 75 cc. of nitric acid (1.20 sp. gr.) are cautiously added, and a gentle heat is applied until all action ceases. If chromium is present it will be necessary to boil the solution after the first reaction is over in order to dissolve the chromium carbide which will be slowly dissolved as the acid concentrates. When the sample is completely dissolved, the solution is rapidly evaporated until a slight scum forms on the surface, when the beaker and contents are cooled slightly and 75 cc. of concentrated nitric acid are added. The contents of the beaker are stirred and heat is applied until incipient boiling ensues. Five grams of potassium chlorate crystals are cautiously added in successive small portions and boiling continued for five minutes, when the beaker and contents are cooled. The solution is filtered with the aid of suction through a plug of asbestos, previously washed with concentrated nitric acid. As some grades of asbestos are slightly soluble in concentrated acids, it should be repeatedly treated with strong hydrochloric acid before being used as a filtering medium. The beaker, to which small portions of manganese tenaciously adhere, and the asbestos plug are washed with concentrated nitric acid (free from nitrous fumes) until the washings are colorless. After the final washing, another flask is substituted for the one containing the filtrate, the filtering tube is filled with a warm five per cent solution of ammonium bisulphite and allowed to stand for one minute. In order to prevent loss of solution, due to effervescence which frequently occurs at this point, it is a good practice to place a cover glass over the filtering tube. The solution of the manganese dioxide is hastened by raising the cover glass and gently agitating the solution with a stirring rod. By successive treatments with ammonium bisulphite, the manganese dioxide is completely dissolved and, after washing the plug with hot water until free from manganese solution, the contents of the flask are transferred to the No. 4 beaker in which the precipitation was effected. Ten cc. of concentrated nitric acid are added, and the solution is boiled until free from sulphur dioxide, generated by the decomposition of the ammonium bisulphite. The solution is cooled, and ammonia is added until a slight permanent precipitate forms, when 15 cc. of a 20 per cent solution of ammonium acetate are added. The solution is boiled for two minutes, filtered into a No. 5 beaker, and the filter and contents are washed twice with hot water. The precipitate is dissolved with dilute nitric acid, and the solution returned to the beaker in which the precipitation was effected. A second precipitation and filtration is made as outlined. The filtrates are combined, 5 cc. of strong acetic acid are added, followed by 10 cc. of a ten per cent solution of ammonium phosphate, and the solution is brought to the boiling point. With constant stirring, strong ammonia is added slowly until a permanent opalescence ensues, at which point the addition of ammonia is discontinued, and the solution vigorously stirred until the characteristic crystalline precipitate of ammonium manganese phosphate is well defined. The addition of ammonia is then continued drop by drop, with constant stirring, until a total of 25 cc. has been added. After the precipitate has settled, it is collected upon an 11 cm. filter paper and washed with two per cent ammonia water until free from soluble salts. The filter paper and residue are ignited in a weighed porcelain crucible at a low temperature until the paper has disappeared, then at a high temperature for 15 minutes. The increase in weight of the crucible multiplied by the factor 38.69 and divided by the initial weight of the sample, is equivalent to per cent manganese.

The manganese pyrophosphate may be contaminated with a trace of silica and in order to correct for this impurity, the residue in the crucible is treated with hydrochloric acid (1–2); heat is applied, and when the manganese pyrophosphate has dissolved, the insoluble silica is removed by filtration, ignited, and weighed. This weight is deducted from the total weight of the residue and the difference is calculated to per cent manganese.

If tungsten is present, the tungstic acid is removed as described under the methods for the determination of tungsten. The filtrate is concentrated and the hydrochloric acid is removed by boiling with strong nitric acid until chlorine is no longer expelled. The solution is then evaporated to a volume of 10-15 cc., 75 cc. of strong nitric acid are added and the manganese is precipitated with potassium chlorate and the analysis finished as above described.

If chromium is present in large quantities, the sample will dissolve so slowly in nitric acid that it is recommended to add also 20 cc. of strong hydrochloric acid. When the sample is dissolved, the determination can be finished as above described after the excess hydrochloric acid has been expelled by boiling, following repeated additions of strong nitric acid.

SODIUM BISMUTHATE METHOD. *ABSENCE OF CHROMIUM.*

This method is very accurate and is, therefore, especially recommended for the determination of manganese in the standards used in the methods hereinafter described. Two precautions, however, may be emphasized; namely, the final oxidation of the manganese by means of sodium bismuthate must be made in the presence of a solution containing 30 to 40 per cent of concentrated nitric acid, and nitrous oxide fumes, organic matter, and chlorides must be excluded, for traces of these substances in the titrating solution vitiate the result.

One gram of the steel contained in a small Erlenmeyer flask is treated with 35 cc. of nitric acid (1.20 sp. gr.). Heat is applied until the steel has dissolved. The solution is then slightly cooled and, in order to oxidize the organic matter, small quantities of sodium bismuthate are successively added until the pink color of permanganic acid persists or the brown oxide of manganese is precipitated upon boiling. Hydrogen peroxide (3 per cent) or ammonium bisulphite (5 per cent) is now added, a few drops at a time, until the manganese dioxide is dissolved, when the excess of the reducing reagent is expelled by continued boiling. Ammonium persulphate may be substituted for bismuthate for oxidizing the organic matter; in this case the excess persulphate is destroyed by boiling.

The solution is cooled rapidly to room temperature, diluted to a volume of 50 cc., an excess of sodium bismuthate, from .5 to 1 gram, is added, and the mixture is immediately agitated thoroughly by vigorous shaking. The solution is decanted through an asbestos filter, and the beaker and filter washed with 3 per cent nitric acid until the washings are colorless. The filtrate and washings are then transferred to a No. 2 beaker. A measured excess of approximately 10 cc. of a thirtieth normal ferrous sulphate solution is now added and the excess thereof determined by a thirtieth normal potassium permanganate solution. The difference between the volume of permanganate solution required and that equivalent to the total volume of ferrous sulphate solution added, is multiplied by the percentage of manganese in one cc. of the standard permanganate solution. The result thus obtained furnishes the percentage of manganese in the sample.

If tungsten is present, the tungstic acid is removed as described under the methods for the determination of tungsten. The filtrate is concentrated and the hydrochloric acid is removed by boiling with strong nitric acid until chlorine is no longer expelled. The solution is then evaporated to a volume of 15 cc., diluted to 50 cc. and the determination completed as above described.

Solutions Required.

Sodium Oxalate Solution.

Sodium Oxalate	1 gram.
Water	1000 cc.

Thirtieth Normal Potassium Permanganate Solution.

Potassium Permanganate	1.06 grams.
Water	1000.00 cc.

The solution is allowed to stand for 24 hours before standardizing. For this purpose 100 cc. of the sodium oxalate solution are transferred to a No. 3 beaker containing 20 cc. of sulphuric acid (one part acid to one part water by volume). The contents of the beaker are heated to 80° C., and the standard permanganate solution is added slowly at first and then rapidly until a permanent pink tint is obtained. The percentage of manganese in one cc. of the standard permanganate solution is found by the following calculation:

$$\frac{1.6397}{\text{(Volume of permanganate solution required to oxidize 100 cc. of the sodium oxalate solution.)}}$$

Thirtieth Normal Mohr's-Salt Solution.

Mohr's-Salt	13.1 grams.
Water	1000.0 cc.

MODIFIED BISMUTHATE METHOD.

Two-tenths gram of the sample is transferred to a No. 2 beaker, treated with 15 cc. nitric acid (1.20 sp. gr.) and boiled until all action ceases. One hundred cc. of hot water are added followed by a small excess of sodium bismuthate. The solution is boiled for one minute, set aside until clear and the excess sodium bismuthate and tungstic acid, if present, are removed by filtration, using an asbestos plug and suction. The filter is washed once with cold water; the filtrate is transferred to a beaker and titrated with standard sodium arsenite solution to the disappearance of the pink color.

If chromium is present, this element will be oxidized to chromic acid, but in the titration the disappearance of the pink tint can be easily noted under these conditions.

SOLUTION REQUIRED.

Standard Sodium Arsenite Solution. See Zinc Oxide Method—Sodium Arsenite Titration.

ZINC OXIDE SEPARATION. *PRESENCE OF TUNGSTEN.*

One gram of the sample contained in a No. 3 beaker is treated with 35 cc. of sulphuric acid (1–6), and heat is applied until all action ceases. Ten cc. of water containing .5 gram of ammonium persulphate are then added to oxidize the iron and the solution is boiled until the excess of persulphate is decomposed. The solution is cooled to room temperature, diluted to 100 cc., almost neutralized with strong ammonia, and then transferred to a 250 cc. graduated flask. Zinc oxide emulsion is added in excess, which is shown when the supernatant liquid appears milky. The solution is then diluted to the mark and thoroughly mixed. The contents of the flask are decanted through a dry filter paper and 50 cc. portions of the filtrate corresponding to .2 gram of the sample may be used for the following determinations:

COLOR METHOD.

A 50 cc. portion of the solution referred to above is transferred to a small beaker or test tube, 10 cc. of strong nitric acid are added and the solution is boiled for several minutes. Fifteen cc. of silver nitrate solution and one gram of ammonium persulphate are then added, and the solution is heated until the pink permanganic acid is developed. The solution is cooled, transferred to a comparison tube and the color matched against a suitable standard which has been treated in exactly the same manner. The relative volume of the solution required to match the color of the standard is equivalent to hundredths per cent manganese.

SODIUM ARSENITE TITRATION.

A 50 cc. portion of the filtrate referred to above is transferred to a suitable beaker, 10 cc. of strong nitric acid are added, and the solution is boiled for several minutes. Fifteen cc. of silver nitrate solution followed by approximately one gram of ammonium persulphate are added and the solution is heated until the pink color of permanganic acid is developed. The solution is then cooled, ten cc. of sodium chloride solution are added to decompose the silver nitrate and, after stirring, standard sodium arsenite solution is added until one drop just dispels the pink tint of permanganic acid. The addition of sodium chloride is unnecessary if the solution of permanganic acid is quite cold and the titration is conducted rapidly; otherwise the excess of persulphate will react upon the reduced manganese with a resulting recurring end point.

SOLUTIONS REQUIRED.

Sodium Chloride Solution.

Sodium Chloride	2.5 grams.
Water	1000 cc.

Silver Nitrate Solution—Stock Solution.

Silver Nitrate	66.5 grams.
Water	1000 cc.

Twenty cc. of the stock solution are diluted to one liter.

Sodium Arsenite Solution—Stock Solution.

Arsenious Acid	10 grams.
Sodium Carbonate	30 grams.
Water	1000 cc.

The water used should be boiling. Sixty-two and one-half cc. of the stock solution are diluted to one liter, whereby each cc. is equivalent to approximately one-tenth per cent manganese, based on an initial weight of two-tenths gram of the sample. The solution is conveniently standardized by using a steel of known manganese content.

If preferred the sodium arsenite solution may be prepared by dissolving approximately 1.1 gram of C. P. sodium arsenite in one liter of water.

DETERMINATION OF PHOSPHORUS

Tungsten, vanadium and titanium, if present, interfere with the determination of phosphorus by the usual methods. Tungsten is insoluble and must be removed before the phosphorus can be precipitated. Vanadium is partially precipitated with the phosphorus, coloring the phospho-molybdate an orange-red, the depth of color depending on the percentage of vanadium present, while if much vanadium is present, the phosphorus is incompletely precipitated. Titanium is usually present in titanium treated steels in quantities less than .1% and in this case does not interfere with the determination of phosphorus by the usual methods. If present in quantities greater than .1%, its action toward the precipitation of phosphorus is much similar to that of vanadium in that it may not only retard the precipitation of phosphorus but may be precipitated with it. In the methods for the determination of phosphorus where titanium is considered as an interfering element, it may thus be understood that it is present in quantities greater than .1%.

VOLUMETRIC METHODS.

ABSENCE OF TUNGSTEN, VANADIUM AND TITANIUM.

ACID-ALKALI TITRATION.

Two grams of the sample are transferred to an 8 ounce Erlenmeyer flask, 25–50 cc. of nitric acid (1.13 sp. gr.) are added and a gentle heat is applied until all action ceases and a black residue of chromium carbide, if present, is completely dissolved. The greater amount of nitric acid is required when chromium is present. A slight excess of a solution of potassium permanganate is then added, and the solution is boiled until the excess of permanganate is decomposed. A slight excess of a reducing solution is added to reduce and dissolve the precipitated manganese dioxide, and the boiling is continued until the excess of the reducing solution is decomposed. The contents of the flask are cooled to a temperature of 80° C., 50 cc. of ammonium molybdate solution are added and the flask is shaken continuously for five minutes. The yellow precipitate of ammonium phosphomolybdate, after settling, is collected upon a 9 cm. filter paper, washed with 2 per cent nitric acid until free from iron solution and finally with a one per cent potassium nitrate solution until free from acid.

The titration may be conducted in either a No. 2 beaker or the flask in which the precipitation was effected. In the former case, the operator should exercise care in completely removing any precipitate adhering to the flask, while in the latter case, the flask should be thoroughly washed with the potassium nitrate solution until the acid is completely removed.

The filter paper and precipitate are transferred to the titrating vessel and treated with an excess of standard sodium hydroxide solution. The filter paper is macerated with a glass rod, if the titration is conducted in a beaker, or if conducted in a flask, a clean rubber stopper is inserted and the contents shaken vigorously until the paper is disintegrated and solution of the precipitate is complete. The solution is diluted to approximately 100 cc., three drops of phenolphthalein solution are added, followed by the standard nitric acid until the pink color disappears. The sides of the titrating vessel are washed with cold water, and with a final volume of about 150 cc., the titration is completed by adding standard alkali solution until the appearance of a permanent pink tint. Each cc. excess of standard alkali over the standard acid used is equivalent to .01 per cent phosphorus.

SOLUTIONS REQUIRED.

Standard Caustic Soda Solution.

Caustic Soda	6.6 grams.
Water	1000 cc.

The water should be free from carbon dioxide. One cc. of a saturated solution of barium hydrate is added to precipitate traces of carbon dioxide. The solution is then filtered and diluted to a volume of one liter.

Standard Nitric Acid.

Strong Nitric Acid	10 cc.
Water	1000 cc.

The standard acid and alkali solutions are adjusted so that they exactly agree, and 1 cc. is equivalent to one-hundredth per cent phosphorus. For confirming the solutions, the use of a steel of known phosphorus content is recommended.

Ammonium Molybdate Solution.

Molybdic Acid (85 per cent)	65 grams.
Water	142 cc.
Strong Ammonia	143 cc.
Nitric Acid (1.20 sp. gr.)	715 cc.

The molybdic acid is added to the water contained in a suitable flask. The ammonia is then added with rotation of the flask until the molybdic acid is dissolved. The solution is then cooled and added gradually, with constant stirring, to the nitric acid. In order to insure a permanently clear solution, one or two drops of a 10 per cent solution of ammonium phosphate are added; the solution is allowed to stand for 12 hours before filtration, conducted preferably by suction through an asbestos plug.

Phenolphthalein Solution.

Phenolphthalein	1 gram.
Ethyl Alcohol	1000 cc.

Nitric Acid (1.13 sp. gr.).

Nitric Acid (1.42 sp. gr.)	240 cc.
Water	760 cc.

Potassium Permanganate Solution.

Potassium Permanganate	25 grams.
Water	1000 cc.

REDUCING AGENTS.

Ammonium Bisulphite. Five per cent solution.

Ferrous Sulphate Solution.

Ferrous Sulphate	50 grams.
Water	1000 cc.

Potassium Nitrite Solution.

Potassium Nitrite	50 grams.
Water	1000 cc.

Sugar Solution.

Sugar	500 grams.
Water	1000 cc.

A very small quantity of this solution should be used for each determination—not more than 3 or 4 drops.

POTASSIUM PERMANGANATE TITRATION.

The yellow precipitate as above obtained is washed with acid ammonium sulphate solution, or, if desired, dilute sulphuric acid (2 per cent), until free from iron and molybdenum salts. The flask in which the precipitation was effected is then placed under the funnel, and dilute ammonia (one part ammonia and three parts water), sufficient to just dissolve the precipitate is poured over the filter. The filter is then washed with hot water, but care should be exercised that the final volume of the solution does not exceed 25 cc. Seventy-five cc. of sulphuric acid (1–1) are added, and the solution may be reduced in a zinc reductor, or 8 grams of granulated zinc (10 mesh) are added, and the solution is gently boiled until the reduction is complete. The undissolved zinc is then collected on a glass wool filter, and both flask and filter are washed with cold water. To the cold filtrate, standard potassium permanganate solution is added until a slight permanent pink tint is obtained. The volume of the permanganate solution required, multiplied by its value in terms of phosphorus and divided by the initial weight of the sample equals per cent phosphorus.

Solutions Required.

Acid Ammonium Sulphate Solution.

Strong Ammonia	15 cc.
Sulphuric Acid (1-1)	50 cc.
Water	935 cc.

Standard Potassium Permanganate Solution.

Potassium Permanganate	2 grams.
Water	1000 cc.

One cc. equals approximately .0056 per cent phosphorus on a one gram basis. The known phosphorus of a standard steel is used as a basis of standardization.

GRAVIMETRIC METHOD.

ABSENCE OF TUNGSTEN, VANADIUM AND TITANIUM.

WEIGHING AS AMMONIUM PHOSPHOMOLYBDATE.

Two to five grams of the sample are transferred to a glazed porcelain dish with cover glass and 25 to 50 cc. of nitric acid (1.13 sp. gr.) are cautiously added. A gentle heat is applied until all action ceases and a black residue of chromium carbide, if present, is dissolved, when the solution is rapidly evaporated to dryness. The cover glass is removed and the contents of the dish heated with the full flame of an Argand or Bunsen burner until the acid is completely expelled. After cooling, 30 cc. of concentrated hydrochloric acid are added, and a gentle heat is applied until the soluble portion is dissolved. The dish is placed upon a suitable asbestos ring in order to prevent the formation of a crust of separated salts on the sides of the dish, and the solution is evaporated until the first appearance of a film upon the surface of the solution. The dish is then removed from the heat, 10 cc. of concentrated nitric acid are added, and heating is continued for one minute. About 40 cc. of cold water are added and, after stirring, the solution is filtered through an 11 cm. filter paper and the filtrate is retained in a 16 ounce flask. The residue on the filter paper is washed with cold 2 per cent nitric acid until the iron solution is completely removed.

To the filtrate, with a volume of not more than 150 cc., 25 cc. of ammonia water (.90 sp. gr.) are added, and the flask is shaken until the precipitate coagulates. Twenty-five cc. of concentrated nitric acid, which should be sufficient to dissolve the precipitate and allow an excess of 7 to 10 cc., are added. The comparatively large amounts of nitric acid and ammonia are required only when 4 to 5 grams of the sample are used and insure the presence of a sufficient quantity of ammonium nitrate which, together with the excess of nitric acid, is essential for the precipitation of pure crystalline ammonium phosphomolybdate. When smaller quantities of the sample are used, the amount of ammonia may be decreased, but there should always be an excess of nitric acid as prescribed.

The solution is heated to 80° C., 50 cc. of the molybdate solution are added and the flask shaken by hand or machine for five minutes. The yellow precipitate should settle at once and, after standing for one hour, is collected upon a 9 cm. filter paper previously dried for one hour at a temperature of 115° C. and weighed between ground-edge watch glasses. The precipitate and filter are washed four times with 2 per cent nitric acid, dried in the same manner as the paper and weighed. The increase in weight multiplied by 1.64 and divided by the initial weight of the sample is equivalent to per cent phosphorus.

WEIGHING AS MAGNESIUM PYROPHOSPHATE

The yellow precipitate obtained as above described is dissolved from the filter paper with hot ammonium citrate solution, the filter paper is thoroughly washed with hot water and the solution retained in a No. 0 beaker. Five to ten cc. of magnesia mixture are added to the cold solution which is then stirred continuously for five minutes. After standing for not less than 3 hours, the precipitate is transferred to a 9 cm. filter paper or a weighed Gooch crucible and washed with dilute ammonia water until free from soluble salts. The filter paper and precipitate are transferred to a porcelain crucible, and ignition is conducted at a low temperature for 10 to 15 minutes and, finally, at a high temperature for 10 minutes. The increase in weight of the crucible multiplied by 27.87 and divided by the initial weight of the sample is equivalent to per cent phosphorus.

Solutions Required.

Ammonium Citrate Solution.

Citric Acid	50 grams.
Strong Ammonia (.90 sp. gr.)	330 cc.
Water	650 cc.

Magnesia Mixture.

Magnesium Sulphate	84 grams.
Ammonium Chloride	250 grams.
Water	665 cc.
Strong Ammonia	335 cc.

Dilute Ammonia.

Strong Ammonia	200 cc.
Water	800 cc.

PRESENCE OF VANADIUM.

ABSENCE OF TUNGSTEN AND TITANIUM.

Two grams of the sample are transferred to a suitable Erlenmeyer flask, 50-80 cc. of nitric acid (1.13 sp. gr.) are added and a gentle heat is applied until the sample is completely dissolved. A slight excess of a solution of potassium permanganate is then added, and the solution is boiled until the excess of permanganate is decomposed. A slight excess of a reducing solution is added to reduce and dissolve the manganese dioxide and the boiling continued until the reducing agent is decomposed. The solution is then evaporated to a volume of 20 cc. and made just ammoniacal. The precipitated hydrates are dissolved with just the amount of strong nitric acid necessary to effect complete solution, and then 5 cc. are added in excess. The solution is cooled to 15° C., or lower, 50 cc. of a 4 per cent solution of ferrous sulphate are added, followed by 75 cc. of molybdate solution. The solution is then shaken continuously for at least 10 minutes, the precipitate allowed 30 to 45 minutes to settle, and the determination is completed according to any of the volumetric or gravimetric methods hereinbefore described.

The points of vital importance are:

(1) The temperature of precipitation should be held at a point (15° C. or lower) where the nitric acid does not oxidize the excess of ferrous salt or the reduced vanadium before complete precipitation of the phosphorus takes place.

(2) The partial neutralization with ammonia must be made before reduction of the vanadic acid, otherwise the heat of the neutralization causes the oxidation of most of the ferrous iron and reduced vanadium by the nitric acid.

(3) Care must be taken to prevent the action of the oxides of nitrogen, since these substances seem to catalyze the oxidation of the vanadyl salt and may in some cases completely prevent precipitation of phosphorus, owing to the large amount of vanadic acid present.

PRESENCE OF TUNGSTEN. *ABSENCE OF TITANIUM.*

Two grams of the sample are transferred to a porcelain dish provided with a cover glass, and treated with 20 cc. of strong nitric acid and 60 cc. of strong hydrochloric acid. A gentle heat is applied until the sample is completely decomposed, when the contents of the dish are evaporated to dryness. The cover glass is removed and the residue in the dish is baked until the excess of acid is completely expelled. The dish is then cooled and 30 cc. of concentrated hydrochloric acid are added. Heat is applied until the soluble portion is dissolved, when the solution is evaporated to a volume of approximately 10 cc. One hundred cc. of water are added and the contents of the dish are boiled for five minutes. The silica and tungstic acid are then removed by filtration and the filtrate is retained in an Erlenmeyer flask. After washing the filter paper alternately with water and hydrochloric acid (1–1) until free from iron solution, the filtrate is evaporated to a volume of approximately 20 cc. The solution is cooled, made just ammoniacal, the precipitated hydrates are dissolved with just the amount of concentrated nitric acid necessary to effect complete solution and then 5 cc. are added in excess. The further treatment of the solution depends upon whether vanadium is present.

If Vanadium is Absent. The solution is treated for the precipitation of phosphorus according to any of the volumetric or gravimetric methods hereinbefore described.

If Vanadium is Present. The solution is cooled to 15° C. or lower and is treated for the precipitation of phosphorus according to the method—Presence of Vanadium.

PRESENCE OF TITANIUM.

ABSENCE OF TUNGSTEN AND VANADIUM.

FUSION METHOD.

Two grams of the sample are transferred to a suitable evaporating dish and treated with 30 cc. of nitric acid (1.20 sp. gr.). Heat is then applied until all action ceases, when the solution is evaporated nearly to dryness. The contents of the dish are transferred to a platinum crucible, evaporated to dryness and intimately mixed with 10 grams of sodium carbonate. The contents of the crucible are fused for one-half hour over a Bunsen or Meker burner. The fusion is transferred to a beaker containing hot water and heat is applied until it is thoroughly disintegrated. The residue containing the titanic acid is removed by filtration and the filter and contents are washed with hot water containing one per cent sodium carbonate. The filtrate is acidified with hydrochloric acid and evaporated to dryness. The residue is moistened with hydrochloric acid and is then treated with 50 cc. of hot water. The contents of the dish are heated, the solution is filtered into a suitable beaker and is then just acidified with nitric acid.

If phosphorus is precipitated in the presence of a large amount of alkali salts, the precipitate will often be contaminated with molybdic acid; it is thus recommended to separate the phosphorus from the mass of alkali salts. For this purpose a small amount of iron, e. g. .05 gram, the phosphorus content of which is known, is accurately weighed and is treated as described under Volumetric Method, Acid Alkali Titration, up to the point where the phosphorus is precipitated by the molybdate solution. The solution of the steel is added to the beaker containing that of the fusion, a slight excess of ammonia is added to the combined solutions and, after boiling for one minute, the precipitate of iron hydrate containing all the phosphorus is removed by filtration. The precipitate is dissolved with warm nitric acid (1.20 sp. gr.) and the phosphorus is precipitated and determined by any of the gravimetric or volumetric methods hereinbefore described. A correction, of course, is applied for the phosphorus contained in the standard iron.

PRESENCE OF TITANIUM, TUNGSTEN AND VANADIUM.

Two grams of the sample are transferred to a porcelain dish provided with a cover glass, and treated with 20 cc. of strong nitric acid and 60 cc. of strong hydrochloric acid. A gentle heat is applied until the sample is completely decomposed, when the contents of the dish are evaporated nearly to dryness. They are then transferred to a platinum crucible, evaporated to dryness, and intimately mixed with 10 grams of sodium carbonate. The contents of the crucible are fused for one-half hour over a Bunsen or Meker burner. The fusion is transferred to a beaker containing hot water and heat is applied until it is thoroughly disintegrated. The insoluble matter is removed by filtration, and a second fusion is made, which is disintegrated in water, the solution filtered, and the two filtrates are combined. The combined filtrates contain sodium tungstate, vanadate and phosphate. In order to separate the phosphorus, a solution of sodium aluminate is used. This is prepared by transferring 10 grams of sodium hydrate and 2 grams of metallic aluminum to a platinum dish and then carefully adding water until the violent reaction is over. When the aluminum is dissolved, the solution is diluted slightly and then filtered; the filtrate and washings are diluted to a volume of 100 cc. Five cc. of this solution are added to the combined filtrates which are then made slightly acid with hydrochloric acid. The solution is heated to about 60°—70° C., ammonia is added until the solution is slightly alkaline, when the phosphorus will be completely precipitated as aluminum phosphate together with the excess of aluminum. The solution is warmed on the hot plate until the precipitate coagulates, when it is filtered and both filter and contents are washed well with hot water. The residue is dissolved from the filter paper with dilute hydrochloric acid, the paper washed well with hot water and the solution is retained in an 8 oz. Erlenmeyer flask. Ammonia is added until the solution is just alkaline. Nitric acid is then added until the precipitate just dissolves when 5 cc. are added in excess. The phosphorus is precipitated by molybdate solution and determined by any of the optional methods previously described; if the precipitate of aluminum phosphate is suspected of containing vanadium, however, the molybdate precipitation is made as described under "Presence of Vanadium."

DETERMINATION OF SULPHUR.

VOLUMETRIC METHOD.

The evolution method for the determination of sulphur can only be used for steel samples that are soluble in hydrochloric acid (1–1). Tungsten, molybdenum and vanadium are not dissolved by hydrochloric acid, and if they are present in large quantities the gravimetric method must be used. The presence of small quantities of these elements, however, does not interfere.

A simple and convenient apparatus for the determination of sulphur by the evolution method may be constructed with a 16 ounce Florence ring-neck flask and suitably bent glass tubing. The flask is closed by a two-hole rubber stopper equipped with a long funnel or thistle tube and a glass exit tube bent at a right angle. The latter is connected, by means of pure rubber tubing, to a similar tube which extends to the bottom of the absorption vessel. The absorption of the evolved gases may be conducted either in a tall No. 4 beaker in which the subsequent titration is effected, or in a large test tube (preferably 10″x1″).

From 3 to 5 grams of the sample are transferred to the flask, the stopper is inserted, and the flask connected to the absorption vessel. Ten to twenty cc. of the absorbent solution are added to the absorption vessel and diluted to 60 or 200 cc., depending upon whether a test tube or a beaker is employed. Sixty-five cc. of dilute hydrochloric acid are added to the flask, and heat is applied so that a continuous brisk evolution of gases results until the sample is in solution. At this point the heat is increased until the solution of the steel is boiling, and the gases in the flask are completely displaced by the resulting steam. The flask is then disconnected from the absorption vessel.

If the absorption was effected in a beaker, 10 cc. of starch solution are added, the delivery tube is removed and washed alternately with a jet of cold water and dilute hydrochloric acid until free from traces of the absorbent solution or adhering particles of the precipitate. If the absorption was effected in a test tube, its contents are transferred to a No. 4 beaker containing 10 cc. of starch solution, and the tubes are washed as above. It is quite essential, before the iodine solution is added, that a slight excess of acid is present, otherwise, the alkali absorbent solution will combine with the iodine which will not be completely liberated upon subsequent acidification. The solution, after acidification, is diluted to 400 cc. with cold water and is gently stirred. The iodine solution is then admitted from a burette in successive portions, followed by vigorous stirring, until the blue color begins to fade slowly. At this point the iodine solution is added cautiously until the addition of a final drop yields a permanently blue color which does not fade upon continued stirring. Each cc. of iodine solution added is equivalent to .01 per cent sulphur based upon an initial weight of five grams of the sample.

Standard potassium iodate solution instead of iodine may be used as the titrating solution, and, since traces of iodine will volatilize from an iodine solution during warm weather, the iodate solution is the more stable.

SOLUTIONS REQUIRED.

Starch Indicator.

An emulsion of 6 grams of starch in 100 cc. of cold water is cautiously added to a litre of boiling water contained in a suitable flask. After continued boiling for five minutes, the flask and contents are cooled, and 6 grams of zinc chloride in 50 cc. of cold water are added to preserve the solution. After thoroughly mixing, the flask is set aside for 24 hours with occasional shaking. When the heavier particles have settled, the supernatent liquid is carefully decanted into a suitable container.

It is recommended that the starch be added to boiling water, as this tends to lessen the often unavoidable frothing; should frothing occur, however, its subsidence may be affected by playing a jet of air over the surface of the boiling solution.

Standard Iodine Solution.

Potassium Iodide	10.0 grams.
Iodine	4.5 grams.
Water	1000.0 cc.

The iodine and potassium iodide are transferred to a graduated one litre flask, 25 cc. of cold water are added, and the flask shaken until the iodine has dissolved. The solution is then diluted to one litre and set aside for not less than 24 hours before standardizing. A standard steel, the sulphur content of which has been established gravimetrically, is used for standardizing the iodine solution, one cc. of which, after the required adjustment, is equivalent to .01 per cent sulphur based upon an initial weight of five grams of the sample

Standard Potassium Iodate Solution.

Potassium Iodate	1.20 grams.
Potassium Iodide	12.00 grams.
Water	1000.00 cc.

The iodate and iodide are dissolved in 300 cc. of water. This solution is then diluted to one liter. If the iodate solution assumes a brown color after standing, a few drops of potash solution are added. The solution is standardized as the standard iodine solution.

Dilute Hydrochloric Acid.

Strong Acid (1.19 sp. gr.)	500 cc.
Water	500 cc.

ABSORBENTS REQUIRED.

Ammoniacal Cadmium Chloride Solution.

Cadmium Chloride	5 grams.
Water	375 cc.
Ammonia (.90 sp. gr.)	625 cc.

Caustic Alkali Solution.

Caustic Soda or Potash	5 grams.
Water	1000 cc.

Ammoniacal Zinc Sulphate Solution.

Zinc Sulphate	10 grams.
Water	375 cc.
Strong Ammonia (.90 sp. gr.)	625 cc.

GRAVIMETRIC METHOD.

PRESENCE OF TUNGSTEN AND MOLYBDENUM

Three to five grams of the sample are transferred to a No. 4 beaker or a 12 ounce Erlenmeyer flask, 100 cc. of strong nitric acid (1.42 sp. gr.) are added, and a gentle heat is applied. A too violent reaction, which occurs with certain grades of steel, is prevented by placing the beaker in cold water; a loss of incompletely oxidized sulphur is thus avoided.

If chromium is present, especially in large amounts, the steel will dissolve very slowly. In this case 50 cc. of strong hydrochloric acid, in addition to the nitric acid, are added and the contents of the beaker are heated until solution is complete.

When the steel is dissolved, the solution is evaporated to a small volume and, after cooling, 30 cc. of strong hydrochloric acid are added. The solution is again evaporated to a small volume and, after the addition of one gram of sodium carbonate, is transferred to a porcelain dish, evaporated to dryness, and baked at a moderate temperature for 10 minutes. The residue is treated with 40 cc. of strong hydrochloric acid and a gentle heat applied until the soluble portion dissolves. The contents of the dish are then evaporated just to dryness. The residue is treated with 60 cc. of hydrochloric acid (1–1) and a gentle heat is applied until the soluble portion dissolves; 50 cc. of water are then added and the solution is boiled for five minutes. The silica is removed by filtration and the residue on the paper is washed with hydrochloric acid (1–15) until the washings are free from iron solution. The filtrate is then evaporated as in the phosphorus determination, on an asbestos pad with cover glass removed until a slight film begins to form upon the surface of the solution. At this point the dish is removed from the heat and, after the addition of a few drops of concentrated hydrochloric acid (usually 3 drops are sufficient), cold water is added to a volume of 100 cc.

Any silica or a possible trace of tungstic acid are collected upon a 9 cm. filter paper, and the solution is received in a No. 2 beaker. The filter paper is washed with dilute hydrochloric acid (1–15) and cold water until the iron is completely removed, when the washing is conducted with hot water to a final volume of 200 cc. Ten cc. of a ten per cent solution of barium chloride is added to the cold solution, and, after standing for 24 hours with occasional stirring, the precipitated barium sulphate is ready for filtration. The supernatant liquid is decanted through a double ashless 9 cm. filter paper. The precipitate is transferred to the paper by means of a jet of dilute hydrochloric acid (1–15), washed with dilute hydrochloric acid (1–15) until free from iron solution and finally with water until free from chlorides.

The filter and contents are transferred to a weighed platinum crucible, ignited uncovered at a low temperature until the paper disappears, and finally at a high temperature for ten minutes. The increase in weight of the crucible multiplied by 13.74 and divided by the weight of the sample used equals per cent sulphur.

The barium sulphate obtained in the manner just described is sometimes in a very finely divided state and traces are often found in the filtrate and washings. This small amount can be recovered by filtration after the solution has been allowed to stand for 24 hours.

If tungsten is present it will be necessary to slightly vary the above method. Three grams of the sample are transferred to a beaker and treated with 50 cc. of strong nitric acid, followed by 50 cc. of strong hydrochloric acid. A gentle heat is then applied until the sample is decomposed and the tungsten is converted to yellow tungstic acid. The solution is evaporated to a low bulk, 30 cc. of strong hydrochloric acid and one gram of sodium carbonate are added, when the contents of the beaker are transferred to a porcelain dish and evaporated to dryness on a sand bath. The contents of the dish are baked gently for ten minutes, cooled, treated with 60 cc. of hydrochloric acid (1–1) and heated until the soluble portion has dissolved. The solution is then evaporated to a volume of 30 cc., an equal volume of water is added, and the contents of the dish are boiled for five minutes. The tungstic acid is removed by filtration and washed thoroughly with hydrochloric acid (1–10) until free from iron. The filtrate is received in a porcelain dish and after the addition of 30 cc. of strong hydrochloric acid is evaporated to dryness. The residue is dissolved with 30 cc. of strong hydrochloric acid, evaporated as in the phosphorus determination on an asbestos pad with cover glass removed until a slight film begins to form upon the surface of the solution. The contents of the dish are then treated for the precipitation and determination of sulphur as above described.

The residue of tungstic acid and silica, provided the steel contains appreciable amounts of silicon, should be examined for traces of sulphur. The filter and residue are placed in a clean platinum crucible, covered with a layer of sodium carbonate and ignited with a sulphur free flame until the paper disappears. The residue is then fused after the addition of sodium carbonate and a small amount of nitre. The fused residue is dissolved with dilute hydrochloric acid and evaporated to dryness, the silica or tungstic acid removed and the filtrate treated with barium chloride. Should a precipitate form after standing for a sufficient length of time, it is filtered off together with any precipitate that may have formed in the original filtrate and the combined weight added to that already obtained. The operator should ascertain positively that any residue so recovered is barium sulphate.

DETERMINATION OF SILICON.

SULPHURIC ACID METHOD. *ABSENCE OF TUNGSTEN.*

To a porcelain dish provided with a cover, 2.3465 grams of the sample (5 times the factor weight) are transferred and 75 cc. of sulphuric acid (1–6) are added. The contents of the dish are heated until all action ceases, when the solution is rapidly evaporated until fumes of sulphuric anhydride are freely given off. The dish is then cooled, 60 cc. of water are added, and the contents of the dish are heated gently until the soluble salts have dissolved. If molybdenum or vanadium are present, these elements will remain insoluble as a black residue and are now dissolved by boiling the solution after adding several crystals of sodium chlorate. The solution is then filtered through an 11 cm. paper and the residue is washed with hydrochloric acid (1–10) and water until free from iron salts. The paper and contents are transferred to a tared platinum crucible, ignited and weighed. About 3 cc. of hydrofluoric acid and two drops of sulphuric acid are added to the crucible, the contents are carefully evaporated to dryness and then to the expulsion of all fumes. The crucible is heated to full redness, cooled and again weighed. The difference between the two weights, or the loss by volatilization, is the silica. Each milligram loss in weight represents .02 per cent silicon.

Should the sample contain a high percentage of silicon, traces of silica will be dissolved and can only be recovered by re-evaporation of the solution. The filtrate is evaporated until fumes of sulphuric anhydride are evolved, the residue is then redissolved as above described and the recovered silica added to that already obtained.

DETERMINATION OF SILICON AND TUNGSTEN.

These two elements may be separated at the same time, and one sample is thus used for their determination. Three grams of the sample contained in a porcelain dish are treated with 150 cc. of hydrochloric acid (1–1), and the contents of the dish are heated until all action ceases. Ten cc. of nitric acid (1.20 sp. gr.) are then cautiously added and the solution is evaporated to dryness on a sand bath.

The residue is treated with 60 cc. of hydrochloric acid (1–1). Heat is applied until the soluble portion dissolves, when the contents of the dish are evaporated to a volume of approximately 30 cc. An equal volume of water is added, the solution is boiled for five minutes, and then filtered through an 11 cm. filter paper. The residue is washed thoroughly with dilute hydrochloric acid (1–10) until free from iron. The filtrate may be reserved for the determination of other elements. The filter and contents are dried, ignited in a platinum crucible and weighed. The ignition should be conducted at not too high a temperature lest traces of the tungstic acid be volatilized. The residue consists of silica, tungstic acid, and impurities (ferric oxide, and titanic acid if titanium is present). The residue is covered with hydrofluoric acid, and if titanium is present, 2 drops of sulphuric acid are added. The contents of the crucible are evaporated to dryness, when the crucible is ignited as before. The residue is weighed as tungstic acid and impurities. The loss in weight is silica, which multiplied by the factor 46.93 and divided by the initial weight of the sample used equals the per cent of silicon.

The residue in the crucible is treated with an excess of sodium carbonate, and heat is then applied until it is completely fused. The fusion is removed from the crucible and both are transferred to a No. 2 beaker containing 100 cc. of hot water. The contents of the beaker are boiled until the fusion is completely disintegrated and the sodium tungstate (formed by the fusion) is completely dissolved. The solution is then filtered through a 9 cm. filter paper and the residue on the filter paper (consisting of ferric oxide and sodium titanate) is washed with hot water until the washings are free from tungsten. The residue on the paper is then ignited and weighed as impurity. The difference between this weight and the weight of the tungstic acid plus impurity represents tungstic acid. The per cent of tungsten is calculated by multiplying the weight of tungstic acid by the factor 79.31 and dividing the product by the initial weight of the sample used.

DETERMINATION OF TUNGSTEN.

RAPID METHOD.

Since the presence of tungsten interferes with the majority of the methods for the determination of other elements, and must therefore first be removed, the following method is given for its rapid separation and determination:

One gram of the sample contained in a No. 3 beaker is treated with 50 cc. of hydrochloric acid (1–1). Heat is applied till all action ceases when 100 cc. of water containing .5 gram of sodium chlorate are added, and the solution is boiled until the tungsten is converted to tungstic acid. The tungstic acid is then removed by filtration, and washed with hydrochloric acid (1-10) until the washings are free from iron solution. The filtrate may be retained for the determination of other elements. The paper and residue are transferred to a platinum crucible, ignited at not too great a temperature, and weighed. If the sample contains a large amount of silicon, the residue of tungstic acid may contain traces of silica. In this case the ignited residue is treated with hydrofluoric acid, the excess of which is removed by evaporation, and the residue in the crucible is again ignited and weighed. Since tungstic acid is usually contaminated with traces of iron, 5 grams of sodium carbonate are then added, and heat is applied until the contents of the crucible are fused. The fusion is then leached with water, and the insoluble ferric oxide is removed by filtration, ignited and weighed. The difference between the weight of the ferric oxide and the combined weight of the tungstic acid and ferric oxide represents the tungstic acid. The percentage of tungsten is found by multiplying this weight by the factor 79.31.

This method is not recommended to be used when absolute accuracy is desired, as it tends to give low results. On this account, the combined weight of tungstic acid plus impurity calculated to per cent tungsten, in many cases, represents a more nearly correct percentage than that obtained after purification.

DETERMINATION OF CHROMIUM

CHLORATE METHOD.

One or two grams of the sample are transferred to an eight ounce flask and 30 to 60 cc. of nitric acid (1.20 sp. gr.) are added. The contents of the flask are heated until the separated tungsten, if present, is a clear yellow color, or, if tungsten is absent, until the black residue of chromium carbide is completely dissolved. The solution is then evaporated until a scum of ferric nitrate begins to form, when the flask and contents are cooled and 70 cc. of strong nitric acid are added. The solution is heated to the boiling point, 1 to 2 grams of potassium chlorate are added, and the contents of the flask are evaporated, in order to decompose the excess of chlorate, to a volume of approximately 30 cc. The contents of the flask are then cooled, diluted with water to 100 cc., and the separated manganese dioxide and tungstic acid, if present, are removed by filtration, using an asbestos plug and suction. After washing the plug with water until the washings are colorless, the filtrate is diluted to 300 cc. and cooled. The solution is transferred to a No. 5 beaker and is now ready for the titration. Standard ferrous ammonium sulphate solution is added from a burette until a decided green color is obtained or to the complete disappearance of the yellow, and the volume of the ferrous ammonium sulphate solution added is noted. Standard potassium permanganate solution is then added from a burette until the solution assumes a pink color which does not fade upon continued stirring. If vanadium is present, the pink color will slowly fade owing to the slow reoxidation of the vanadium. When the vanadium is completely oxidized, however, a pink color lasting one minute is obtained, which is taken as the end point. The volume of standard permanganate solution required is then noted. The per cent of chromium is obtained by conducting a blank titration on the ferrous ammonium sulphate solution under the same conditions as outlined under the actual determination. For this purpose the same volume of ferrous ammonium sulphate used in the determination is transferred to a suitable beaker; the contents of the beaker are diluted with water to a volume of 300 cc., standard potassium permanganate solution is then added until a permanent pink color is obtained and the volume of permanganate solution required is noted. The difference in cc. between the volume of permanganate solution required in the blank titration and that required in the actual determination, representing the volume of permanganate equivalent to the chromium in the steel, is multiplied by the value of one cc. of permanganate solution in terms of chromium. The product thus obtained is divided by the weight of sample used and the quotient represents the percentage of chromium in the sample.

Solutions Required.

N/10 Ferrous Ammonium Sulphate Solution.

Ferrous Ammonium Sulphate	39.2 grams.
Water	1000 cc.

N/10 Potassium Permanganate Solution.

Potassium Permanganate	3.17 grams.
Water	1000 cc.

N/10 Sodium Oxalate Solution.

Sodium Oxalate	6.7 grams.
Water	1000 cc.

Fifty cc. of this solution are transferred to a No. 4 beaker, diluted with water to 350 cc., heated to 80° C. and 10 cc. sulphuric acid (1–1) are added. The standard permanganate solution is then added until a permanent pink color is obtained, and the number of cc. required is noted. The value in percentage of one cc. of the permanganate solution in terms of chromium is found by multiplying the factor .1733 by 50 and dividing the product so obtained by the number of cc. of standard permanganate solution required.

PERMANGANATE OXIDATION METHOD.

PRESENCE OF TUNGSTEN.

One or two grams of the sample are transferred to a No. 4 beaker, treated with 70 cc. of sulphuric acid (1–6), and heat is applied until all action ceases. One to two grams of ammonium persulphate are then added and the solution is boiled until the tungsten is completely oxidized and the excess of persulphate is destroyed. While boiling, successive small portions of potassium permanganate solution (4%) are added, until a precipitate of manganese dioxide is formed and remains undissolved after continued boiling. When such a permanent precipitate is obtained, the solution is further boiled for five minutes. If a large excess of permanganate solution was added, the solution of the steel will be colored pink, and, in order to destroy the permanganate, a few crystals of manganese sulphate or 15 cc. of strong nitric acid are added. The contents of the beaker are then boiled until the solution shows a pure yellow color. The solution is cooled, diluted to about 100 cc. and the manganese dioxide and tungstic acid are removed by filtration using an asbestos plug and suction. The plug is washed with hot water until the washings are colorless. The filtrate is diluted to 300 cc., cooled, and the chromium determined by titration, as described under the chlorate method.

PERMANGANATE OXIDATION METHOD.

ABSENCE OF TUNGSTEN.

The precipitated manganese dioxide which is removed by filtration in the method just described may be dissolved by hydrochloric acid, if preferred, as the chromic acid will not be reduced in the presence of dilute hydrochloric acid. The filtration is thus avoided and the addition of crystals of manganese sulphate or strong nitric acid is unnecessary. The solution of the sample, after the oxidation with permanganate, is treated with 10 cc. of hyrdochloric acid (1–1). The solution is boiled until the precipitate is dissolved, and further boiled for about 5 minutes, or until the generated chlorine is expelled. The solution is then diluted to a volume of 300 cc. and the chromium determined by titration, as described under the chlorate method.

DETERMINATION OF CHROMIUM AND VANADIUM.

PERSULPHATE METHOD.

One to two grams of the sample are transferred to an 8 ounce Erlenmeyer flask, and 25 cc. of sulphuric acid (1–3) are added. Heat is then applied until all action ceases, when 6 cc. of nitric acid (1.20 sp. gr.) are added and the solution is boiled until the brown fumes are expelled. Twenty-five cc. of silver nitrate solution are then added and the contents of the flask are diluted to a volume of approximately 175 cc. The solution is heated to boiling, removed from the heat, and 12 cc. of ammonium persulphate solution are added. The chromium oxidizes first, then when the pink color due to oxidation of manganese appears, a few drops of hydrochloric acid (1–2) are successively added, followed by boiling until the pink color of permanganic acid disappears or the brown dioxide is completely dissolved. The solution is then further boiled until the generated chlorine is expelled, when the solution is cooled, diluted with water to about 250 cc. and the chromium is determined by titration as described under the chlorate method. Since the percentage of vanadium in the sample is usually small, it is recommended that N/30 instead of N/10 solutions of potassium permanganate and ferrous sulphate be used.

After the determination of the chromium, the solution will have a slight pink tint which must be destroyed before the vanadium can be determined. For this purpose, one or more drops of N/30 ferrous sulphate solution are added, and, since the excess of permanganate only is thus reduced, it is unnecessary to note the volume of ferrous sulphate added. Before proceeding with the titration, a white porcelain test plate should be prepared by carefully waxing its surface and then spacing upon it single drops of potassium ferricyanide solution (.1%) which will act as an external indicator for the titration. A measured excess of N/30 ferrous sulphate solution is now added—5 cc. is usually sufficient. The vanadic acid is thus reduced, and in order to determine the excess of ferrous sulphate, N/30 potassium bichromate solution is added, a few drops at a time, followed by stirring of the solution. After each addition of the bichromate solution, a test drop is transferred to the test drop on the plate, and the addition of the titrating solution is continued with frequent tests until the green tint of the ferrous iron can no longer be detected, when the two test drops meet. A little practice will soon enable one to satisfactorily note the conclusion of the titration, but since vanadium will rapidly react with the ferricyanide indicator giving it a green color, the end point must be judged immediately after the two test drops meet.

The volume of N/30 potassium bichromate solution required for the titration is noted. The percentage of vanadium is obtained by conducting a blank titration on the ferrous sulphate solution under the same conditions as outlined under the actual determination. To the solution of a plain steel, approximately the same percentage of chromium as that contained in the sample, is added in the form of potassium bichromate. An excess of N/30 ferrous ammonium sulphate solution is then added, followed by N/30 potassium permanganate solution until a pink tint is obtained. This slight excess of permanganate is just dispelled by the addition of one or more drops of N/30 ferrous sulphate solution. The same measured excess of this solution as used in the actual determination is then added, and its value in terms of N/30 potassium bichromate solution is found by titration. The difference in cc. between the volume of potassium bichromate solution required in the blank titration and that required in the actual determination, representing the volume of potassium bichromate equivalent to the vanadium in the steel, is multiplied by the value of one cc. of bichromate in terms of vanadium.

If tungsten is present, the tungstic acid is removed as described under the methods for the determination of tungsten. Twenty cc. of sulphuric acid (1-3) are added, and the solution is evaporated until fumes of sulphuric anhydride are evolved. The residue is then dissolved with water and the determination completed as above described.

SOLUTIONS REQUIRED.

Silver Nitrate Solution.

Silver Nitrate	12.5 grams.
Water	1000 cc.

Ammonium Persulphate Solution.

Ammonium Persulphate	140 grams.
Water	1000 cc.

N/30 Potassium Permanganate Solution; N/30 Potassium Bichromate Solution; and *N/30 Sodium Oxalate Solution:*—See N/10 solutions—"Chlorate Method." These solutions are prepared as the N/10 solutions by using but ⅓ the weights of the respective salts.

N/30 Potassium Bichromate Solution.

Potassium Bichromate	1.637 grams
Water	1000 cc.

This solution is verified by titrating a measured volume of ferrous sulphate solution and is adjusted, as indicated by the titration, so that it is exactly N/30. The vanadium value of 1 cc. of bichromate solution is .17% vanadium.

DETERMINATION OF VANADIUM.

VOLUMETRIC METHODS

Ether Separation.

Three grams of the sample are transferred to a No. 2 beaker and treated with 60 cc. of hydrochloric acid (1.13 sp. gr.). Heat is applied and when the sample is dissolved, the iron is oxidized with 3 cc. of strong nitric acid and the solution is evaporated to a volume of approximately 25 cc. The contents of the beaker are transferred to a separatory funnel, the beaker is washed with hydrochloric acid (1.11 sp. gr.) and the washings are transferred to the funnel. The volume of the solution should not exceed 50 cc. The contents of the funnel are cooled, an equal volume of ether is added and the solution is shaken vigorously. The lower portion of the solution containing the vanadium is drawn off, warmed to evaporate the ether, cooled, and 10 cc. of sulphuric acid (1.84 sp. gr.) are added. The solution is then evaporated until fumes of sulphuric anhydride are given off, when it is cooled and five cc. of potassium permanganate solution (4%) are added to destroy carbonaceous matter and to oxidize any reduced iron. The solution is boiled for one minute, when 30 cc. of strong hydrochloric acid are added. The solution is again evaporated until dense fumes of sulphuric anhydride are evolved. The beaker and contents are cooled, diluted with water to 100 cc., and titrated at a temperature of 40° C. with standard permanganate solution to the appearance of a pink color which persists for one-half minute. The percentage of vanadium is found by multiplying the number of cc. of permanganate solution required for the titration by the value of 1 cc. of permanganate solution in terms of vanadium and dividing the product by the weight of the sample used.

The ether used in making the separation should be the purest that can be obtained. If the ether is not of such high grade, an error may be encountered and, on this account, it is good practice to make a blank determination. This is conducted by dissolving 3 grams of a plain steel and treating it as above described. If a blank is found, a corresponding correction should be applied.

In the presence of tungsten, the tungstic acid is separated as described under the method for the determination of tungsten, the filtrate is concentrated, an ether separation is made and the determination completed as above described.

Solutions Required.

Hydrochloric Acid (1.11 sp. gr.)

Strong Hydrochloric Acid	543 cc.
Water	457 cc.

N/10 Potassium Permanganate Solution.

Potassium Permanganate	3.17 grams.
Water	1000 cc.

N/10 Sodium Oxalate Solution.

Sodium Oxalate	6.7 grams.
Water	1000 cc.

Fifty cc. of this solution are transferred to a No. 4 beaker, diluted with water to 350 cc., heated to 80° C., and then acidified with 10 cc. of sulphuric acid (1–1). The permanganate solution is added until a permanent pink tint is obtained and the number of cc. required is noted. The value in per cent of one cc. of permanganate solution in terms of vanadium is found by multiplying the factor .51 by 50 and dividing the product by the number of cc. of permanganate solution required.

If desired, a weaker permanganate solution may be used for the titration. Fractional weights of sodium oxalate and potassium permanganate may be used and their solutions prepared and the permanganate solution standardized as just described.

Phosphomolybdate Precipitation.

Two grams of the sample are transferred to an 8 ounce Erlenmeyer flask and treated with 50 cc. of nitric acid (1.20 sp. gr.). Heat is applied until the sample is dissolved, when the solution is treated with an excess of potassium permanganate solution (4%) and then boiled until the excess of permanganate is decomposed. A slight excess of ammonium bisulphite solution (5%) is added to reduce and dissolve the precipitated manganese dioxide and the solution is boiled until the excess of bisulphite is decomposed. Two and one-half cc. of ammonium phosphate solution (10%), and 10 grams of ammonium nitrate, followed by 100 cc. of ammonium molybdate solution are then added and the flask is shaken for 5 minutes. The phosphorus is thus precipitated as ammonium phospho-molybdate, the large quantity of which carries down completely the vanadic acid present.

When the precipitate has subsided, the supernatant liquid is decanted upon an asbestos filter and the solution is filtered with the aid of suction. The precipitate is retained in the flask and is washed by decantation, 3 times, with hot acid ammonium sulphate solution. The precipitate retained on the filtering plug is dissolved therefrom with hot concentrated sulphuric acid—30 cc. should be sufficient—and the solution is returned to the flask containing the main precipitate. The flask and contents are then heated until the precipitate is completely dissolved, when 10 drops of strong nitric acid are added and the heating is continued until fumes of sulphuric anhydride are evolved. The flask is removed from the heat, cooled, and the vanadium is reduced by successive small additions, followed by shaking, of hydrogen peroxide. When the solution assumes a deep brown color, the flask is again heated until fumes of sulphuric anhydride are evolved for one minute. The solution should now be a deep green color; if this is not the case the vanadium has not been completely reduced, so additional peroxide is added and the solution is again heated until fumes of sulphuric anhydride are evolved for one minute. The flask and contents are then cooled, 150 cc. of water are added, and the vanadium is titrated at a temperature of 70°–80° C. with potassium permanganate solution.

If tungsten is present, the tungstic acid is removed as described under the methods for the determination of tungsten. The filtrate is concentrated and the hydrochloric acid is removed by boiling with concentrated nitric acid until chlorine is no longer expelled. The solution is then evaporated to a volume of 10–15 cc. and the vanadium determined as above described.

SOLUTIONS REQUIRED.

Acid Ammonium Sulphate Solution.

Strong Ammonia	15 cc.
Sulphuric Acid (1–1)	50 cc.
Water	1000 cc.

Standard Potassium Permanganate Solution.

This solution is prepared and standardized as described under the "Ether Method."

Ammonium Molybdate Solution.

This solution is prepared as described under "Determination of Phosphorus—Acid-alkali Titration."

COLOR METHOD. *ABSENCE OF TITANIUM.*

This method furnishes a rapid and convenient means for determining vanadium in steel; the success of the method, however, as in all color determinations depends upon the use of suitable steel standards. The standards are prepared by drilling or planing pieces of steel, rolled or cast, and their vanadium content is determined by the methods hereinbefore described.

As chromium and nickel impart a green color to the solution of a steel sample, it is quite essential that the standard should contain approximately the same percentage of these elements as the test to be compared. Special standards should, therefore, be prepared to fit the various requirements.

One gram of the sample, contained in a 4 ounce flask, is treated with 40 cc. of sulphuric acid (1–4). Heat is applied until the sample is dissolved, when 5 cc. of nitric acid (1.20 sp. gr.) are added and the solution is boiled until brown fumes cease to be evolved. Ten cc. of ammonium persulphate solution (5%) are then added to oxidize the organic matter and the solution is boiled for about 3 minutes or until the excess of the persulphate is decomposed. The solution is then cooled to room temperature and 5 cc. of hydrogen peroxide are added, when a deep brown color due to vanadium will be developed. One gram of a standard vanadium steel is treated in a manner identical to the sample and when the brown color of the vanadium is completely developed, the solution is transferred to a comparison tube and diluted with water so that each cc. or a convenient multiple of the vanadium value of the standard in cc. represents one-hundredth per cent vanadium. The solution is then thoroughly mixed. The solution of the sample is transferred to a similar comparison tube and its color matched against that of the standard by viewing the solution in a camera, or before a white surface. The total number of cc. of the solution of the sample required to match the solution of the standard, or the quotient obtained by dividing it by the multiple used for the dilution of the standard is equal to per cent vanadium.

If tungsten is present, this method may be used after the tungstic acid is separated as described under the "methods for the determination of tungsten." To the filtrate 20 cc. of sulphuric acid (1–1) are added and the solution is evaporated until dense fumes of sulphuric anhydride are evolved. The residue is dissolved in hot water, 5 cc. of nitric acid (1.20 sp. gr.) are added, and the solution is boiled for a few minutes. The determination is then completed as above described.

Solutions Required.

Hydrogen Peroxide Solution.

Sodium Peroxide	7 grams.
Sulphuric Acid (1–1)	250 cc.
Water	750 cc.

DETERMINATION OF NICKEL.

VOLUMETRIC METHOD.

ABSENCE OF COPPER AND COBALT.

One gram of the sample is transferred to a No. 3 beaker and treated with 30 cc. of nitric acid (1.20 sp. gr.). Heat is then applied and when the sample is almost dissolved, 10 cc. of strong hydrochloric acid are added. The contents of the beaker are again heated until the sample is completely dissolved, when the solution is concentrated to a volume of 10 to 15 cc. The contents of the beaker are cooled and 50 cc. of a solution of citric and sulphuric acids are added, followed by strong ammonia until the solution is just alkaline to litmus, when an excess of 3 cc. is added. The neutralization of the solution should be made as soon as possible after the addition of the citric acid as the latter may reduce traces of iron, which condition would interfere with the titration of the nickel. The solution is cooled to room temperature, and, after the addition of 2 cc. of potassium iodide solution (5%), the solution is ready for the nickel titration. From a burette 3 cc. of standard silver nitrate solution are added to the beaker, when a precipitate of silver iodide will be formed. Standard potassium cyanide solution is then slowly added with constant stirring until the precipitate is just dissolved and the solution is perfectly clear. Standard silver nitrate solution is again added, followed by standard potassium cyanide solution, until the solution is again clear. Alternate additions of the standard solutions are made until the cloudiness of the solution due to the addition of 2 drops of the standard silver nitrate is just dispelled by the final addition of 2 drops of the standard cyanide. Each cc. excess of standard cyanide solution over standard silver nitrate solution required for the titration, represents .1% nickel.

A little trouble may be encountered by one using this method for the first time due to the presence of the large amount of iron which slightly retards the end point. A little practice, however, will soon enable one to satisfactorily note the conclusion of the titration. A more distinct end point will be obtained if the sample is dissolved and an ether separation of the iron made as described under "Determination of Vanadium—Ether Method." The acid portion, after being boiled to expel the ether, is treated with 5 cc. of the citric and sulphuric acid solution, and the determination concluded as above described.

For the majority of alloy steels, 50 cc. of the citric and sulphuric acid solution will be found sufficient; however, if the sample contains a high percentage of chromium or vanadium, it may be necessary to use twice this amount.

If tungsten is present in large quantities, the tungstic acid should be separated as described under the "methods for the determination of tungsten." The filtrate is concentrated and the determination completed as above described. Small amounts of tungsten do not interfere.

Solutions Required.

Standard Silver Nitrate Solution.

Silver Nitrate	5.7926 grams.
Water	1000 cc.

Standard Potassium Cyanide Solution.

Potassium Cyanide	4.5 grams.
Water	1000 cc.

The silver nitrate solution is carefully prepared and the cyanide solution adjusted to exact agreement therewith. For this purpose, to a No. 3 beaker containing 100 cc. of water, 3 cc. of strong ammonia and 2 cc. of potassium iodide solution (5%), there is added from a burette 30 cc. of the silver nitrate solution. Standard potassium cyanide solution is then added until the solution is perfectly clear. The volume of the cyanide solution required is noted, and the cyanide solution is adjusted so that the standard solutions are in exact agreement. With exactly agreeing solutions, each cc. excess of standard cyanide solution over the silver nitrate solution should correspond to .1 per cent of nickel. The value of the solutions should then be confirmed by titrating a standard nickel steel, the nickel content of which has been determined gravimetrically by the subsequently described glyoxime method.

Sulphuric and Citric Acid Solution.

Citric Acid	200 grams.
Sulphuric Acid (1–1)	200 cc.
Water	800 cc.

GLYOXIME METHOD.

One gram of the sample is transferred to a No. 3 beaker and treated with 35 cc. of hydrochloric acid (1–1). Heat is then applied and when the sample is almost dissolved 3 cc. of strong nitric acid are added. The contents of the beaker are again heated until the sample is completely dissolved, when the solution is concentrated to a volume of 10 to 15 cc. The contents of the beaker are then cooled and 40 cc. of a solution of tartaric or citric acid (20%) are added.

Since the steel may contain silicon, and the citric and tartaric acids are often contaminated with insoluble foreign matter, it is a good practice to filter the solution at this point. The solution is then diluted to a volume of 350 cc., and strong ammonia is added until it is just alkaline, when it is heated to the boiling point, and 10 cc. of dimethylglyoxime solution are added for each per cent of nickel present. The contents of the beaker are stirred for one minute, cooled, and then set aside for thirty minutes. The bright red precipitate of nickel dimethylglyoxime quickly subsides and the nickel can then be determined by any of the optional methods hereinafter described.

If cobalt is present in large amounts as in cobalt steels, the conditions necessary for making this determination must be slightly varied. The nickel must be precipitated in the cold, as otherwise, it is either but partially precipitated or is accompanied by an organic compound of iron and cobalt. Thus, in the presence of cobalt, to the solution of the steel, there is added the same amount of citric acid as above prescribed, and the solution is diluted to a volume of 350 cc.; strong ammonia is then added until just alkaline, when the solution is again cooled. Ten to twenty cc. of dimethylglyoxime solution for each per cent of nickel present are added, followed by 1 cc. of strong ammonia, drop by drop and with constant stirring for one minute. The solution is set aside for 15–30 minutes, when the precipitate of nickel is removed by filtration and determined by any of the optional methods hereinafter described. Should there be any doubt as to the purity of the precipitate so obtained, it should be dissolved in nitric acid, the solution boiled for one minute, and the nickel reprecipitated as previously described. Proportionately smaller amounts of citric acid and dimethylglyoxime should be used in the reprecipitation. Nickel in the presence of cobalt can also be determined if the majority of iron is removed and the nickel precipitated as described under the method "Determination of Cobalt–(Ni.)".

If tungsten is present in small amounts, it does not interfere; if present in large amounts, it should be removed as described under the methods for the determination of tungsten. The nickel can then be determined in the filtrate by this method.

Weighing the Precipitate.

The solution is filtered through a 9 cm. filter paper previously dried for one hour at a temperature of 110°–115°C. and weighed between ground-edge watch glasses. The filter and contents are washed six times with hot water, when they are dried in the same manner as the paper and weighed. The increase in weight multiplied by the factor 20.31 furnishes the per cent nickel.

WEIGHING AS NICKEL OXIDE.

The solution is filtered and the precipitate retained on an 11 cm. filter paper. The paper and contents are washed six times with hot water, transferred to a weighed platinum crucible, and then ignited and weighed. The increase in weight represents nickel oxide, 78.57 per cent of which represents nickel.

BY TITRATION.

The precipitate is dissolved with nitric acid and the solution boiled for five minutes. The nickel is then determined by titration as described under "Volumetric Methods." Since the solution is free from iron, the addition of sulphuric-citric acid is unnecessary.

SOLUTION REQUIRED.

Dimethylglyoxime Solution.

Dimethylglyoxime	10 grams.
Ethyl Alcohol	1000 cc.

DETERMINATION OF COBALT—(NI.)

SULPHIDE PRECIPITATION.

One gram of the sample contained in a No. 3 beaker, is treated with 100 cc. of hydrochloric acid (1.11 sp. gr.). Heat is then applied until all action ceases, when the contents of the beaker are diluted with an equal volume of water containing .5 gram of sodium chlorate. The contents of the beaker are boiled, with stirring, until any metallic residue is dissolved, or until the tungsten, if present, is converted to tungstic acid. The tungstic acid is removed by filtration and the filter and contents are washed with hydrochloric acid (1–10) until the washings are free from iron. To the filtrate retained in a No. 3 beaker, 5 cc. of nitric acid (1.20 sp. gr.) are added, and the solution is evaporated to a volume of approximately 40 cc. The solution is cooled and transferred to a separating funnel with the aid of hydrochloric acid (1.11 sp. gr.). The volume of the solution should not exceed 50 cc. Forty cc. of ether are then added to the beaker and transferred to the funnel. The funnel is stoppered and the solution vigorously shaken several times. When the ethereal solution containing most of the iron has separated, the lower liquid is drawn off into the same beaker in which the steel was dissolved. The funnel is allowed to stand for five minutes and the small quantity of the acid solution which accumulates in the point of the funnel is added to the solution in the beaker. The beaker and contents are heated at a low temperature to expel the traces of ether. When the odor of ether can no longer be detected, 100 cc. of water containing 5 grams of citric acid are added, and the solution is then neutralized with strong ammonia with final addition of 5 cc. in excess.

The solution is diluted to 200 cc. and saturated with hydrogen sulphide gas, when the iron, cobalt, nickel and traces of manganese will be precipitated as sulphides. The precipitate is removed by filtration, retained on an 11 cm. filter and the filter and contents are washed 3 times with water containing hydrogen sulphide. The funnel should be kept covered as much as possible in order to exclude air. The paper and contents are transferred to a platinum crucible, dried and carefully roasted, and finally ignited at a high temperature for twenty minutes.

The residue in the crucible is transferred to a No. 2 beaker, dissolved in 50 cc. of strong hydrochloric acid, and diluted with water to a volume of 150 cc. The solution is neutralized with ammonia and 10 cc. are added in excess.

One-half gram of ammonium persulphate is added and the solution boiled for a few minutes. The precipitated oxides of iron and manganese are removed by filtration, washed with water, dried, ignited and weighed. The difference in weight between this weight and that of the total oxides represents the cobalt and nickel oxides. The filtrate containing the nickel and cobalt retained in a No. 3 beaker, is boiled until a slight excess of ammonia remains. The solution is then cooled to 70°C., 5 cc. of a one per cent alcoholic solution of dimethylglyoxime are added, when the beaker and contents are cooled to room temperature and allowed to stand for one-half hour. The precipitate of nickel is removed by filtration and the percentage of nickel determined by any of the previously described methods. The difference between the weight of nickel oxide and the combined weight of nickel and cobalt oxides, represents the cobalt oxide (CO_3O_4). The weight of cobalt oxide multiplied by 73.44 equals the per cent of cobalt.

If copper is present, traces of this element will be precipitated by ammonium sulphide, consequently the copper should be removed after the ether separation by saturating the solution with hydrogen sulphide gas. The filtrate is then boiled until the hydrogen sulphide is expelled, and the nickel and cobalt are determined as above described.

SOLUTION REQUIRED.

Hydrochloric Acid (1.11 sp. gr.)

Strong Hydrochloric Acid	543 cc.
Water	457 cc.

NITROSO-β-NAPHTHOL METHOD.

Two grams of the sample are transferred to a No. 3 beaker and treated with 50 cc. of strong hydrochloric acid. A gentle heat is applied and when all action ceases the iron and any metallic residue is oxidized with 10 cc. nitric acid (1.20 sp. gr.), or sodium chlorate—1 gram. The solution is evaporated until the salts just begin to separate. The contents of the beaker are slightly diluted in order to insure solution of all soluble salts, transferred to a graduated 500 cc. flask and cooled to room temperature. Zinc oxide emulsion is added in excess, which is shown when the supernatant liquid appears milky. The contents of the flask are diluted to the mark, mixed well, and the flask is set aside until the heavy precipitate has settled. Two hundred and fifty cc. of the filtered solution (equivalent to one gram of the sample) are transferred to a No. 5 beaker, and, after the addition of 5 to 8 cc. of strong hydrochloric acid, diluted to a volume of 350 cc.

The solution is heated to the boiling point and is then ready for the precipitation of the cobalt. A solution of nitroso–β–naphthol must first be prepared by dissolving this compound in glacial acetic acid in the proportion of one gram to 10–15 cc. of the acetic acid. To the boiling solution of the sample, there is then added, for each .025 gram of cobalt present, a volume of the solution of the reagent corresponding to one gram of the reagent.

The cobalt will be precipitated as a red colored compound, together with a portion of the excess of the reagent, and, after stirring, the beaker is set aside until the precipitate has settled. The hot solution is then filtered, the filter and contents are washed twice alternately with hydrochloric acid (1–1) and water, and finally with hot water 8 times. The precipitate is transferred to a porcelain crucible, heated gently until the carbonaceous matter has disappeared, and then at a high temperature for 20 minutes. The crucible is cooled, weighed, and the percentage of cobalt is found by multiplying the weight of the residue (CO_3O_4) by the factor 73.44

DETERMINATION OF COPPER.

ABSENCE OF MOLYBDENUM.

Five grams of the sample are transferred to a glazed porcelain dish, 65 cc. of nitric acid (1.20 sp. gr.) are added and the covered dish is heated until solution is practically complete. Twenty-five cc. of sulphuric acid (1–1) are then added and the solution is evaporated until fumes of sulphuric anhydride are evolved. Ten cc. of sulphuric acid (1–1) are added followed by 50 cc. of hot water, when a gentle heat is applied until the separated salts are dissolved. The solution is filtered; the filter is washed six times with hot water, and the filtrate is retained in a No. 4 beaker. The filtrate is diluted to 300 cc., heated to boiling and, after the addition of 25 cc. of concentrated ammonium bisulphite solution, the boiling is continued to the complete reduction of the iron. Thirty cc. of a 20% solution of sodium hyposulphite are then added, and the boiling is continued for five minutes, or until the precipitated copper has coagulated. The precipitate is collected upon an 11 cm. filter, washed with dilute nitric acid (2%) and hot water, and the copper may be determined by the gravimetric or volumetric method described below.

If preferred, the sample may be dissolved with sulphuric instead of nitric acid. In this case, 5 grams of the sample are transferred to a No. 5 beaker, 150 cc. of sulphuric acid (1–5) are added and heat is applied until the sample is dissolved. Since the iron is in the reduced state, the addition of ammonium bisulphite is unnecessary. The solution is diluted to a volume of 300 cc., and the copper is precipitated with hyposulphite and the determination concluded as above described.

If tungsten is present, the tungstic acid is separated as described under the methods for the determination of tungsten. To the filtrate, 20 cc. of sulphuric acid (1–1) are added, when the solution is evaporated to fumes of sulphuric anhydride. The residue is dissolved with 10 cc. of sulphuric acid (1–1) and 50 cc. of hot water. The solution is diluted to a volume of 300 cc., and is treated with ammonium bisulphite and thiosulphate for the precipitation of copper as above described. If both the tungsten and copper are present in large quantities, traces of copper may be held by the tungstic acid. This small amount of copper can be separated from the tungstic acid by fusing with 5 grams of sodium carbonate. The fusion is leached out with hot water and the insoluble residue containing the copper is removed by filtration and added to the main precipitate of copper.

GRAVIMETRIC METHOD.

The filter containing the precipitate is carefully ignited and weighed. Too great a temperature in the ignition causes the copper oxide to fuse to the crucible. Since copper oxide is somewhat hyrgoscopic, care should be observed that the residue in the crucible does not absorb moisture from the air.

The ignited copper oxide carries with it traces of contaminating iron, and possibly titanium. If it is desired to correct this error, the impure oxide is dissolved in the crucible with 10 cc. of strong nitric acid, the solution is transferred to a No. 2 beaker and diluted to 100 cc., when the iron and titanium are removed by an ammonia precipitation. The precipitate so obtained is collected upon a 9 cm. filter, washed with hot water, ignited in the crucible in which the previous ignition was conducted and the weight noted. The weight is deducted from the weight of the impure copper oxide and the difference represents pure copper oxide. The per cent of copper is calculated by multiplying the weight of pure copper oxide by the factor 79.90 and dividing the product by the weight of the sample used.

VOLUMETRIC METHOD.

The nitric acid solution of the impure copper oxide in the No. 2 beaker obtained as above described, is rapidly evaporated to the smallest volume possible in order to remove the bulk of the free acid, and the solution is diluted with cold water to a volume of 150 cc. Strong ammonia is then added from a burette until the addition of a final drop causes the permanent blueing of the solution, after which there is added by means of a pipette six drops of acetic acid. Ten cc. of a 40 per cent solution of potassium iodide are added and the standard sodium hyposulphite solution is run in until the color of the liberated iodine has almost disappeared. Ten cc. of the starch solution are now added and the addition of the standard sodium hyposulphite solution is continued to the final disappearance of the blue. The number of cc. of the hyposulphite solution required multiplied by its value in terms of copper and divided by the weight of the sample used equals the per cent copper in the sample.

The apparently large excess of potassium iodide is employed because of its relation to the final end point in the titration, the sharpness of which decreases in proportion as the excess of the iodide is decreased. The presence of ammonium salts in the solution also tends to lessen the permanency of the end point, hence, the necessity for the preliminary evaporation of the acid solution.

SOLUTIONS REQUIRED.

Starch Solution.

See Starch Solution—"Determination of Sulphur."

Standard Sodium Hyposulphite Solution.

Sodium Hyposulphite	8 grams.
Water	1000 cc.

One cc. of the standard solution is equal to approximately .002 gram of copper. The solution may be standardized by using a standard copper steel, the copper content of which has been determined by the gravimetric method. Or the solution may be standardized by titrating, as above described, a nitric acid solution of approximately .05 gram of pure copper, accurately weighed.

PRESENCE OF MOLYBDENUM.

One to five grams of the sample are transferred to a No. 4 beaker and treated with 25 cc. to 125 cc. of sulphuric acid (1–4). When all action has ceased, 2 to 10 grams of ammonium persulphate are added to dissolve the separated molybdenum, and the contents of the beaker are boiled until solution is complete, and the excess of persulphate is destroyed.

The solution is cooled, almost neutralized with ammonia, diluted to 250 cc. saturated with hydrogen sulphide, and then boiled until the sulphides of copper and molybdenum coagulate. The precipitate is collected upon a filter and washed several times with cold water containing hydrogen sulphide. The filter and contents are transferred to a weighed porcelain crucible and ignited at a very low heat until the paper is completely destroyed, thus converting the sulphides to oxides. The crucible is cooled and to the residue consisting of copper oxide, molybdic acid, traces of ferric oxide and titanic acid if titanium is present, there are added 10 cc. of sulphuric acid (1–1). The crucible and contents are heated until fumes of sulphuric anhydride are freely given off, and, after cooling, the contents of the crucible are transferred to a No. 2 beaker containing 50 cc. of water. The solution is made slightly alkaline with caustic soda and saturated with hydrogen sulphide, whereby the copper and iron are precipitated as sulphides. The contents of the beaker are filtered and the copper is determined gravimetrically or volumetrically as previously described.

If tungsten is present, the tungstic acid is separated as described under the "Methods for the Determination of Tungsten," and the filtrate is evaporated to fumes of sulphuric anhydride after the addition of 30 cc. of sulphuric acid (1–1). The contents of the dish are treated with 50 cc. of water and heated until the residue is dissolved and the solution is then treated as above described.

DETERMINATION OF MOLYBDENUM.

One gram of the sample contained in a suitable beaker is treated with 60 cc. of sulphuric acid (1–4). Heat is applied until all action ceases, when two grams of ammonium persulphate are added to dissolve the separated molybdenum. The contents of the beaker are boiled until solution is complete and the excess of persulphate is destroyed. The solution is diluted to 250 cc., almost neutralized with ammonia, and then saturated with hydrogen sulphide. The contents of the beaker are boiled, thus coagulating the sulphides of molybdenum, copper if present, traces of iron, and titanic acid if titanium is present. The precipitate is separated by filtration, washed with water containing hydrogen sulphide and the paper and contents are transferred to a weighed porcelain crucible and ignited at a temperature just sufficient to completely burn the filter. The sulphides are thus converted to oxides and the molybdenum is determined by any of the optional methods described below.

If tungsten is present, it is separated as described under the "Methods for the Determination of Tungsten," the filtrate is evaporated to fumes of sulphuric anhydride after the addition of 30 cc. of sulphuric acid (1–1). The contents of the dish are treated with 50 cc. of water and heated until the residue is dissolved and the solution is then treated as above described.

GRAVIMETRIC METHODS.

Weighing the Molybdenum Trioxide.

The crucible containing the ignited oxides is weighed. Ten cc. of a 10% solution of sodium hydroxide are added and a gentle heat is applied until the molybdenum trioxide is dissolved. The contaminating oxides remain undissolved and, after diluting with water, are removed by filtration, washed with hot water until free from alkali, and the paper and contents are ignited in the same crucible in which the oxides were previously ignited. The increase in weight represents the contaminating oxides, and the difference between the weight of total oxides and the contaminating oxides is the molybdenum trioxide. This weight multiplied by 66.67 equals the per cent molybdenum.

Weighing as Lead Molybdate.

The alkaline solution of molybdenum trioxide obtained as described above is acidified with acetic acid; 30 cc. of a 5% solution of lead acetate are added and the solution is boiled for five minutes. The solution is set aside until the precipitate settles, when the lead molybdate is filtered on asbestos contained in a Gooch crucible. The filter and precipitate are washed with hot water, ignited, cooled and weighed as lead molybdate. This weight multiplied by 26.15 equals the per cent molybdenum.

VOLUMETRIC METHOD.

The alkaline solution of molybdenum obtained as above described is acidified with 10 cc. of sulphuric acid (1.84 sp. gr.), diluted or evaporated to a volume of 100 cc., and heated, if necessary, almost to the boiling point. The solution is then reduced by passing through a zinc reductor or 8 grams of zinc 20 mesh are added and the solution warmed for a few minutes. The undissolved zinc is collected upon a glass wool filter and both flask and filter are washed with cold water. The molybdic acid is reduced approximately to the sesquioxide and the cold solution is titrated with a standard potassium permanganate solution to the appearance of a pink color.

SOLUTIONS REQUIRED.

N/10 Potassium Permanganate Solution.

Potassium Permanganate	3.17 grams.
Water	1000 cc.

The solution is standardized with the use of a standard molybdenum steel, the molybdenum content of which has been determined gravimetrically. The standardization should be conducted as outlined under an actual determination.

UNIV. OF CALIFORNIA

DETERMINATION OF ALUMINUM.

Five grams of the sample contained in a No. 5 beaker are treated with 50 to 60 cc. of strong hydrochloric acid. Heat is applied until the sample is dissolved, when the solution is diluted to about 350 cc. and heated to boiling. Two grams of sodium phosphate are added, and with continued boiling, dilute ammonia (1–1) is added, a few drops at a time, until a slight turbidity appears. The solution is cleared with the least possible quantity of hydrochloric acid (1–1), and 3 cc. are added in excess. Ten to fifteen cc. of acetic acid (99.5%) and 10 grams of sodium hyposulphite are added and the solution is boiled for 15 minutes. All the aluminum is precipitated with certain amounts of chromium, nickel and copper if these elements are present. The solution is filtered while warm and washed well with hot water. The residue is ignited in a platinum crucible and fused with 2 grams of sodium carbonate and one-half gram of pure graphite if chromium is present. The graphite is added to prevent the oxidation of the chromium. The fusion is leached in water and the insoluble residue collected on a filter paper, ignited, and fused as before. This fusion is leached in water, the solution is filtered and the two filtrates, containing the aluminum, are combined. To the combined filtrates there are added 2 grams of sodium phosphate, 5 grams of ammonium chloride and 15 cc. of strong hydrochloric acid. The solution is heated to 60° to 70°C., is made just alkaline with ammonia, and is then allowed to stand at this temperature for 1 to 2 hours. The precipitate is removed by filtration, washed 8 times with hot water, ignited in a porcelain crucible and weighed as aluminum phosphate. This weight multiplied by .2219 and divided by the weight of the sample taken equals the per cent aluminum. As the reagents often contain traces of aluminum, a blank determination should be made as outlined above, and a correction applied to the percentage of aluminum found.

If tungsten is present, 2 grams of the sample are treated with 40 cc. of hydrochloric acid (1–1). When all action ceases, 5 cc. of strong nitric acid are added to oxidize the iron and tungsten, and the solution is digested on a hot plate until the tungstic acid is a pure yellow color. The tungstic acid is removed by filtration and the filtrate is retained in a No. 5 beaker. As the residue on the filter may contain traces of alumina, the paper and contents are transferred to a No. 2 beaker and treated with ammonia (1–3) just sufficient to dissolve the tungstic acid. The alumina is insoluble, and is removed by filtration, dissolved with hot hydrochloric acid (1–1) and the solution is added to the main filtrate. The aluminum is then determined in this solution as above described.

If molybdenum is present, an ether separation is made as described under "Determination of Vanadium—Ether Method." The molybdenum is thus retained by the ether. The lower layer of the solution, containing the aluminum, is transferred to a No. 5 beaker, boiled to expel traces of ether, and the aluminum is determined as above described.

UNIV. OF CALIFORNIA

DETERMINATION OF TITANIUM.

COLOR METHOD.

ABSENCE OF VANADIUM, CHROMIUM, TUNGSTEN, MOLYBDENUM AND NICKEL.

One gram of the sample is transferred to a No. 2 beaker and treated with 15 cc. of sulphuric acid (1-3). Heat is applied until the sample is dissolved, when five cc. of nitric acid (1.20 sp. gr.) are added to oxidize the iron. The solution is then boiled until the brown fumes have disappeared.

A plain steel free from titanium is used for the standard and is treated exactly as the sample. The solutions of the sample and standard are cooled to room temperature. The solution of the sample is transferred to a comparison tube, 5 cc. of hydrogen peroxide are added, when the whole is diluted to a volume of 50 cc. and mixed. Into a similar tube are placed 5 cc. of hydrogen peroxide; the solution of the standard is transferred thereto and the contents of the tube are diluted to a volume slightly smaller than the solution of the sample. Standard titanium sulphate solution is now added from a burette till, after thorough mixing, the color matches that of the solution of the sample, when the standard solution is diluted to the same volume, again thoroughly mixed, and its color compared with the solution of the sample. The determination is completed by carefully matching the colors after the addition, if necessary, of one or more drops of the standard solution. The number of cc. of the standard titanium sulphate solution used indicates the titanium present.

SOLUTION REQUIRED.

Hydrogen Peroxide Solution.

Sodium Peroxide	7 grams.
Sulphuric Acid (1–1)	250 cc.
Water	750 cc.

The sodium peroxide is added to the sulphuric acid in successive small portions. After each addition the solution is cooled to room temperature.

Standard Titanium Sulphate Solution.

Twenty-six hundredths of a gram of ignited titanic acid is fused with six grams of sodium carbonate; the fusion is disintegrated in 50 cc. of water and the crucible and lid are placed therein. After warming for an hour with 100 cc. of dilute sulphuric acid (1-4), solution will usually be complete. This solution is transferred to a 250 cc. volumetric flask and diluted to the mark with water. The purity of the titanic acid may be found, and the solution thus standardized by precipitating 50 cc. of the solution with sodium thiosulphate as described under the gravimetric method. One cc. of this solution should equal approximately .6 milligram of titanium.

GRAVIMETRIC METHOD.

Five grams of the sample contained in a No. 3 beaker are treated with 100 cc. hydrochloric acid (2–1) and the contents of the beaker are boiled until all action ceases. One hundred cc. of water containing 3 grams of sodium chlorate are then added in order to oxidize or dissolve any separated metallic residue, and the contents of the beaker are boiled until the tungsten (if present) is converted to yellow tungstic acid. The solution is diluted to a volume of 200 cc. and boiled for 5 minutes. The tungstic acid is then separated by filtration and washed with hydrochloric acid (1–10) until the washings are colorless. The filtrate is retained in a No. 5 beaker.

The tungstic acid may hold traces of titanium, which are recovered by treating the residue with ammonia (1-3). The tungstic acid is thus dissolved while the titanium will remain insoluble, and is separated by filtration. This residue is reserved to be added to the main precipitate of titanium obtained as follows:

To the main filtrate a slight excess of ammonium bisulphite is added to reduce the iron, followed by ammonia till the acid solution is almost neutralized, when 15 cc. of ammonium acetate (20%) and 5 cc. of glacial acetic acid are added. The solution is then boiled for 5 minutes whereby the titanic acid is precipitated with probable traces of aluminum, chromium, iron and vanadium. The precipitate is removed by filtration and is washed three times with hot water. This precipitate is combined with the one reserved as above described and ignited in a platinum crucible, when a fusion is made with 3 grams of sodium carbonate. A few particles of potassium nitrate are then added to oxidize the chromium, and the fusion is continued for 5 minutes. The fusion is leached with water and the insoluble residue of ferric oxide and sodium titanate is removed by filtration.

The residue on the filter paper is dissolved in hot hydrochloric acid (1–1), the titanium is reprecipitated as above described, removed by filtration, and ignited and weighed in a platinum crucible. The increase in weight multiplied by 60 and divided by the weight of sample taken, represents titanium.

If tungsten, molybdenum and vanadium are absent, the oxidation with sodium chlorate is unnecessary and the method can therefore be considerably shortened by omitting this procedure. In this case the majority of the iron will not be oxidized, and consequently there is added a much smaller quantity of ammonium bisulphite, after the addition of which the determination is completed as above described.

THIS BOOK IS DUE ON THE LAST DATE
STAMPED BELOW

AN INITIAL FINE OF 25 CENTS

WILL BE ASSESSED FOR FAILURE TO RETURN THIS BOOK ON THE DATE DUE. THE PENALTY WILL INCREASE TO 50 CENTS ON THE FOURTH DAY AND TO $1.00 ON THE SEVENTH DAY OVERDUE.

NOV 29 1935

LD 21-100m-7,'33

QD133
U7

320978

U.S. steel

UNIVERSITY OF CALIFORNIA LIBRARY